PYROLYSIS OF POLYESTERS;
A STUDY OF SATURATED MODEL COMPOUNDS.

by

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SYNOPSIS.

Methyl and ethyl esters of saturated dibasic acids were chosen as models to represent saturated segments of a co-polyester chain, giving a contrast of the effects of presence and absence of β-hydrogen on the alkyl group.

It was observed that not only does absence of β-hydrogen confer a higher thermal stability but that it entirely alters the pyrolytic decomposition. Alkyl-oxygen scission, the predominant breakdown route of the ethyl esters, did not occur in the methyl compounds. Surprisingly, methylene-chain rupture was the principal reaction of the latter, an α:β-unsaturated ester being formed. The decomposition is complex and mechanisms are considered.

A series of acid anhydrides, related to the esters studied, were also examined, yielding interpretations of secondary decomposition in the pyrolyses of esters. Perhaps the most notable feature was the formation of unsaturated monobasic acids from cyclic anhydrides by elimination of carbon monoxide. A discussion of reaction mechanisms is included.

TABLE OF CONTENTS.

Tables.

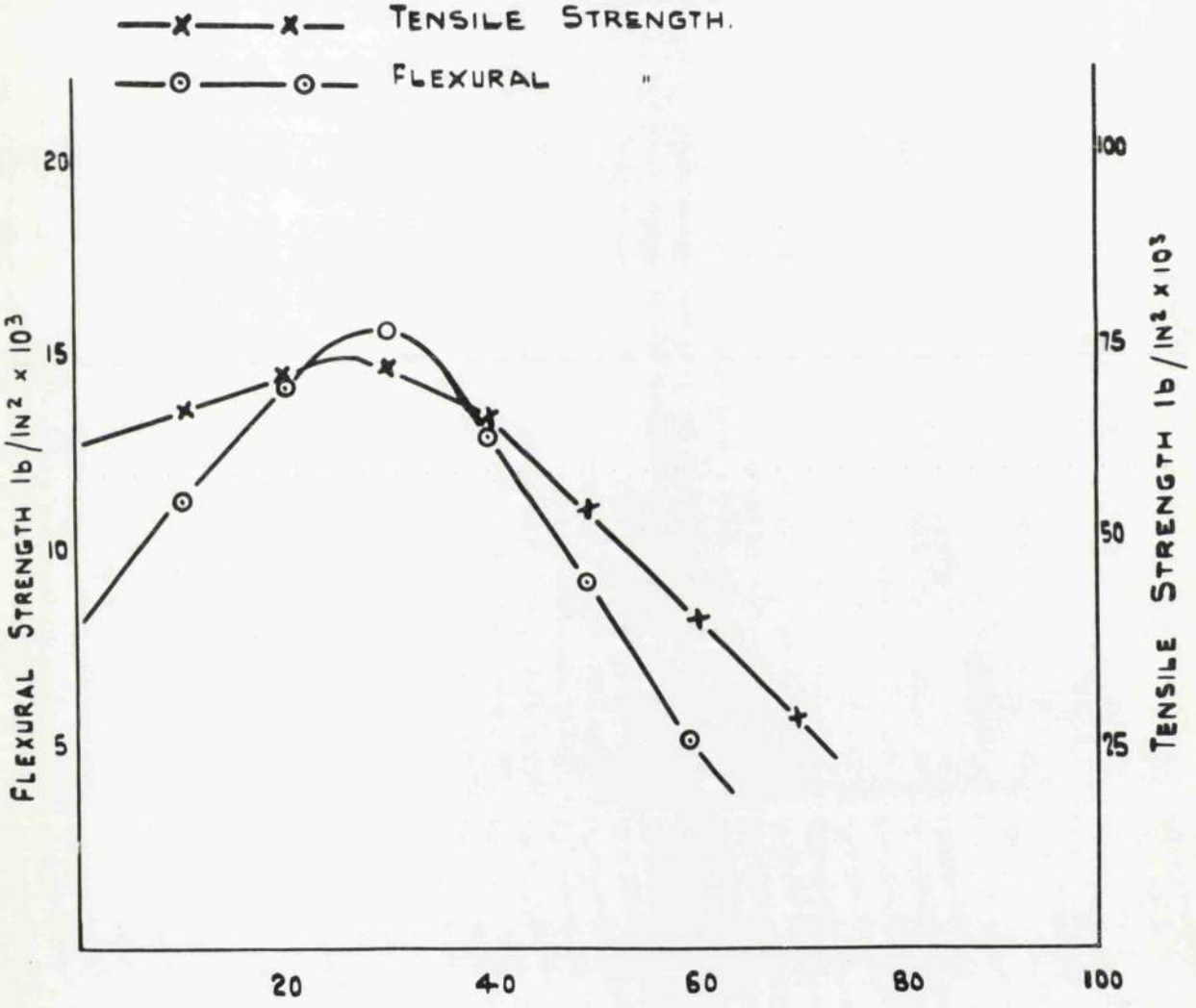
Figures.

1. INTRODUCTION.

Commercial polyester resins are prepared from an unsaturated dibasic acid and a dihydric alcohol and moulded at low pressure by copolymerisation with a vinyl monomer. Maleic acid or anhydride are most generally used to provide the unsaturated centres(1) by condensation with ethylene glycol, smaller quantities of saturated dibasic acids being incorporated.

Ethylene fumarate and maleate were first prepared by Vorländer(2), 1894, but it was not until 1929 that Carothers and Arvin(3) described them as polyesters and confirmed the property of hardening on heating(4). Soon after that polyesters were introduced as surface coatings, the hardening being regarded as a combination of further condensation and crosslinking(5). The first copolymers, with styrene, vinyl acetate and methyl α-methylacrylate, were reported by Bradley, Kropa and Johnstone(6), 1939. Relatively long curing times were required and darkening of the resins occurred. These difficulties were overcome and commercial production commenced in 1940. The output of cast resins rose from 3.5 to 28.0 million pounds per annum between 1948 and 1953(1) showing the rapid expansion of the industry. A wide variety of colours is now available and much progress has been made in tailoring of the physical properties by selection of suitable vinyl monomer(7) or inclusion of saturated acids in the polyester

PROPERTIES OF POLYPROPYLENE MALEATE / ADIPATE – 30% STYRENE.



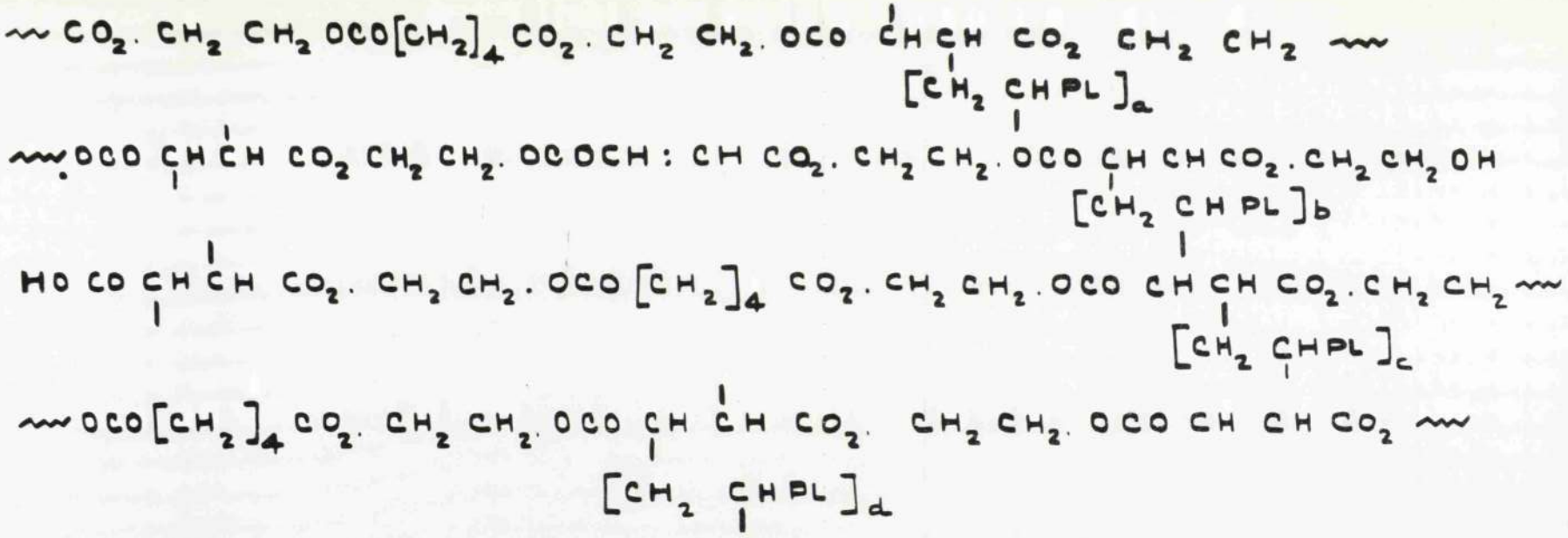
[PARKES AND MOFETT (12)]

FIG. 1

chain(8). Specialised resins have such properties as fire-resistance(9) and high electrical conductance(10).

Resins based on ethylene glycol/maleic anhydride polyester have been most widely studied. Feuer(11) has found the structure to have a trans, fumarate configuration, indicating isomerisation during the condensation. The most satisfactory combination of physical and chemical properties is obtained when the acid number is 25 - 50(75). Saturated acids are employed mainly to improve the flexibility of the moulded product but Parkes and Mofett(12) examining the effects of varying ratios of saturated to unsaturated acid groups found optimum compositions for maximum improvement of tensile and flexural strength, illustrated by Fig. I.

The main defect of these resins is the low maximum working temperature. Above 250° there is a marked loss of mechanical strength, while at 300° use would be limited to very short periods(76). The present work is part of a fundamental study, by Ritchie et al.(13,14), of the thermal decomposition of poly(ethylene fumarate) crosslinked with an unsaturated momomer, by the technique of model compounds representing segments of the macromolecule, Fig. II. Esters of succinic, adipic and sebacic acids have been chosen as saturated models.



REPRESENTATION OF POLY (ETHYLENE FUMARATE / ADIPATE)

PARTIALLY CROSS-LINKED WITH STYRENE.

a, b, c, d = 15 - 25

FIG. II

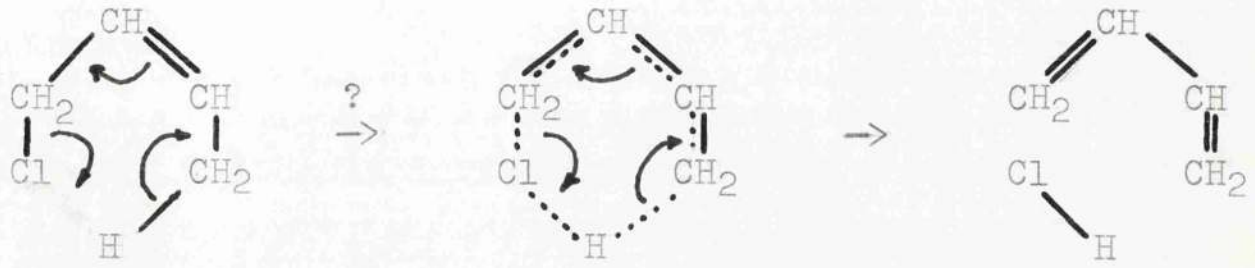
1.1. Pyrolysis.

1.1.1. General.

Hurd(15) has described the process as "the transformation of a compound into another substance or into other substances through the agency of heat alone." Catalytic effects have been excluded as far as possible using an all glass apparatus. Carbonisation which accompanies most pyrolyses, to a greater or lesser extent, was believed to affect the breakdown(16,17) but recent work by Bailey et al.(20), Royals(19) and Depuy et al.(18) has shown no qualitative nor significant quantitative effects. Metallic catalysis has increased in importance with the application of high molecular weight esters in the high temperature lubrication of gas turbines. This is being examined in the vapour phase by Muir and Ritchie(21) and in the liquid phase at the Royal Aircraft Establishment, Farnborough(22).

Two important general rules for the prediction of probable routes of pyrolysis have been advanced. The Rule of Least Molecular Deformation was proposed by Peytral(23), while more recently Rice and Teller(24) stated the Principle of Least Motion. Both yield the same results, therefore only the latter is discussed. It states that a purely thermal reaction will be favoured when a) there is a maximum gain in resonance energy in the transition state and b) there is a minimum change in the electronic configuration. The

Principle has been successfully applied to many decompositions. Elimination of hydrogen chloride from 1-chlorobut-2-ene(24) provides a good illustration;



Here the conditions of minimum electronic displacement and maximum resonance are fulfilled by the postulated transition compound.

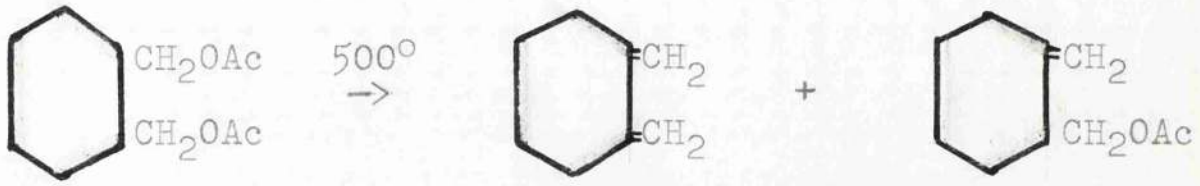
Many compounds undergo pyrolysis by two or more simultaneous competitive routes(25,26,27). Norris(26) found n-butane to yield methane and propene at 375°, while at 438° ethylene accompanies these gases.

It was concluded that temperature had a controlling infleunce over competitive reactions. Hurd and Blunk agreed with this, attributing the complex pyrolysate from methyl esters to the high temperature required to induce decomposition.

1.2. Pyrolysis of Esters.

The thermal decomposition of esters has been very widely studied as a preparative method for complex olefinic compounds. A striking example is the formation of 1:2-dimethylene-

4-cyclohexane(29).



A patent exists for the preparation of unsaturated acids from β-alkoxy-saturated acids(30).

$$AcOCH_2CH_2CO_2H \xrightarrow[1\ \%\ \text{hydroquinone}]{180^\circ} AcOH + CH_2{:}CHCO_2H$$

Mild conditions are sufficient and the inhibitor prevents polymerisation.

Work in these laboratories has been concerned with competitive reactions of model compounds representing segments of a polyester chain. Ethylene dibenzoate, a model of polyethylene terephthalate, undergoes a two-route breakdown(27), thus;

$$BzOCH_2CH_2OBz \xrightarrow{500^\circ} \begin{cases} BzOH + CH_2{:}CHOBz \\ MeCH(OBz)_2 \end{cases}$$

A further example of complex breakdown is afforded by methyl acetate(25).

$$AcOMe \longrightarrow \begin{cases} AcOH + \tfrac{1}{2}CH_2{:}CH_2 \\ MeCHO + CH_2O \end{cases}$$

1.2.1. Nomenclature.

The known routes of ester decomposition have been described by Ritchie(12) and the following nomenclature, which is used throughout, proposed.

Alkyl-oxygen Scission - A type.

Elimination of an olefin from the ester yields the parent acid by a hydrogen transfer.

$$RCO_2CR'_2CHR''_2 \rightarrow RCO_2H + R'_2C{:}CR''_2$$

Secondary and tertiary alkyl groups give mixtures of olefins.

Acyl-oxygen Scission - B type.

Rupture of the acyl-oxygen bond is favoured by the absence of hydrogen on the β-carbon of the alkyl group. Two aldehydes or an alcohol and a keten may be formed, hydrogen migration being possible in two directions.

Elimination - C type.

Direct loss of carbon monoxide or dioxide from an ester is included, also decarbonylation of an aldehyde but acid decarboxylation is not thus classified.

Disproportionation - D type.

This is the well known reaction of an asymmetrical molecule decomposing to products of greater symmetry.

Rearrangement - R type.

Reactions yielding a single product isomeric with the pyrolysand are termed rearrangements.

Intra-acyl Scission.

In this novel type of thermal breakdown, reported by Mackinnon and Ritchie(31), scission occurs between the carboxyl and alkyl groups of the acid, thus;

$$CH_2{:}CHCO_2Ph \rightarrow CH{:}CH + HCO_2Ph$$

1.2.2. Alkyl-oxygen Scission.

A^1 type.

The presence of an available hydrogen on the β-carbon of the alkyl group is essential and when this condition is fulfilled the major fraction of the decomposition occurs by this route.

$$RCO_2CR'_2CHR''_2 \rightarrow RCO_2H + R'_2C{:}CR''_2 \quad \ldots A^1$$

The temperatures at which decomposition occurs have been studied by Hurd and Blunck(28). Tertiary esters gave A^1 scission in the region of 225°, while primary esters required much more vigorous conditions. A kinetic examination by Maccoll(32) showed a progressive increase in the relative rates of decomposition from primary to tertiary.

	Relative rates of decomposition		
	Et	Pr^i	Bu^t
Acetate	1	26	515
Formate	1	20	720

It is seen that the acid has little effect.

Only a single olefin may be formed from a primary ester, but mixtures of isomers may be produced from secondary and tertiary compounds. The Hofmann Rule(28) suggests that the least substituted olefin would be formed preferentially. Thus but-1-ene would be expected to be the exclusive unsaturated product from sec-butyl acetate.

$$AcOBu^{s} \rightarrow AcOH + CH_2{:}CHEt \quad \ldots A^1$$

However, a mixture of butenes is obtained(35). An electron-withdrawing substituent affects the direction of elimination and according to the Saytzeff Rule(33) the more highly alkylated olefin should be formed. (-)-Menthyl benzoate gives benzoic acid and the olefins (+)-p-menth-2-ene and (+)-p-menth-3-ene in the ratio of 1:2 in the liquid phase(34), the conclusion being that the Saytzeff Rule held under these conditions. A series of pyrolyses of tert-amyl acetate at temperatures ranging from 225° to 600° yielded both possible pentenes(18).

$$AcOCMe_2Et \rightarrow AcOH + \begin{matrix} CH_2{:}CHMeEt \\ + \\ Me_2C{:}CHMe \end{matrix} \quad \ldots A^1$$

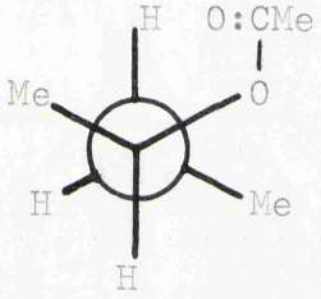
The interesting feature was that in the liquid phase the Saytzeff Rule was obeyed but the quantity of 2-methylbut-1-ene increased with temperature, predominating at 600°. Thus a single compound may react in accordance with both rules but at different temperatures. A change from a cyclic to an ionic mechanism was proposed as a possible explanation.

Some recent papers have questioned the specificity of direction of elimination(19,35) on the evidence of more accurate measurements by gas-liquid chromatography. Assuming a completely random system, Depuy et al.(35) calculated by statistical methods the expected yields of isomers from a

number of sec- and tert- esters. Experimental figures were in close agreement with the theoretical values, as illustrated for sec-butyl acetate, thus;

				found	calc.
$AcOBu^s$	$\xrightarrow{450^\circ}$	AcOH	+	$CH_2{:}CHEt$	57 %	60 %
				MeCH:CHMe	43 %	40 %

The trans form of but-2-ene predominated. The cyclic transition states, shown by the Newman projections, were used to account for this.



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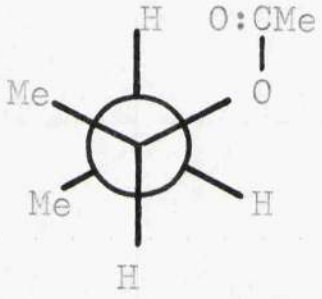


II

An eclipsing effect of the methyl groups in II explains the lower yield of the cis olefin.

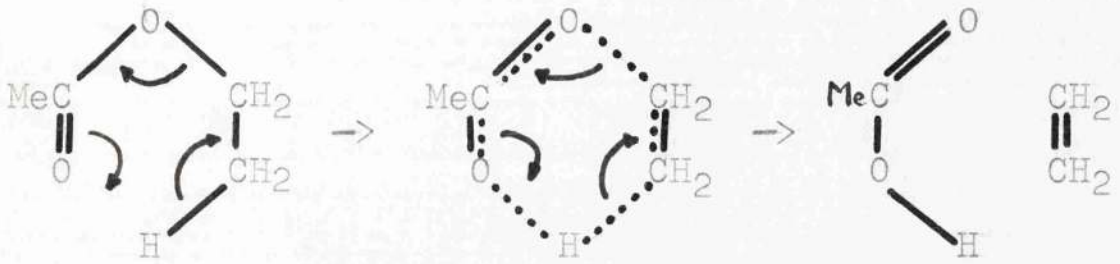
Alicyclic esters having a 1-methyl substituent are formally capable of giving both endo- and exo- cyclic olefins. A general preferance for the formation of the less strained form has been found(18,36,37).

			found
1-methylcycloheptyl acetate	$\xrightarrow{+}$	1-methylcycloheptene	76 %
		methylenecycloheptane	24 %

Ring size does not appear to alter the relative proportions significantly(18).

Hurd and Blunck(12) proposed a cyclic mechanism for

A^1 scission, involving transfer of the β-hydrogen. A simple illustration can be made with ethyl acetate, thus;



Although critised by Houtman et al.(38) on the lack of evidence for the existence of hydrogen bonds at high temperatures, this mechanism is now generally accepted. Barton, Head and Williams(34) proved the exclusive A^1 scission of (-)-menthyl benzoate to be unimolecular and cis-elimination to be preferred, both facts being consistent with the cyclic transition state. Further support is obtained from the pyrolysis of 1:2-dimethylcyclohexyl acetate(35). The cis form gives 28 % 1:2-dimethylcyclohex-1-ene, while the blocking effect of the methyl groups prevent its formation from the trans compound.

A^o type.

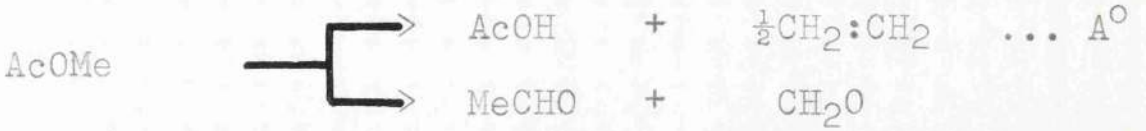
A form of alkyl-oxygen scission is possible when there is no hydrogen on the β-carbon.

$$RCO_2CHR'_2 \rightarrow RCO_2H + \tfrac{1}{2}CR'_2{:}CR'_2 \quad \ldots A^o$$

Combination of two alkyl groups gives the olefin.

Few examples of this reaction have been recorded and the reaction is usually of a minor nature, as in the breakdown

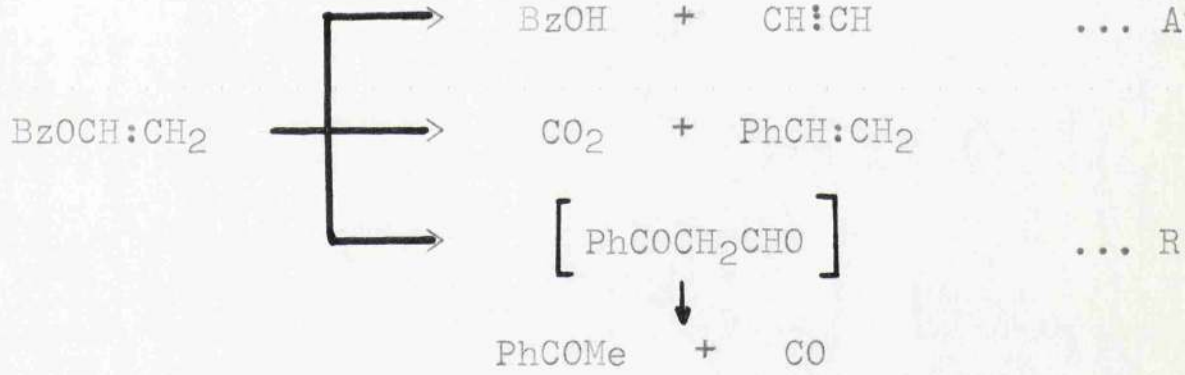
of methyl acetate(25).



The mechanism is uncertain but the high temperatures required would seem to contradict a molecular reaction.

A^2 type - Alkenyl-oxygen Scission.

This is the analogous reaction of alkenyl esters to the A^1 scission of the saturated compounds, an alkyne and an acid being formed. It is a minor route in the decomposition of vinyl benzoate(27) and of the vinyl chlorobenzoates(39).



The cyclic mechanism of the A^1 scission would be consistent with the findings while the conjugative effect of the double bond would lower the resonance energy of the transition state, accounting for the minor nature of the reaction.

1.2.3. Acyl-oxygen Scission.

Rupture of the acyl-oxygen bond gives two fragments, hydrogen migration being necessary to give stoichiometric products. This can take place in two directions, each of which is considered separately.

B^1 type.

A keten and an alcohol are the primary products.

$$>CHCO_2CHR_2 \rightarrow >C{:}CO + HOCHR_2 \quad \ldots B^1$$

This is not a common reaction and does not usually occur in the presence of a β-hydrogen. Phenyl acetate, in which the structure precludes A^1 scission, decomposes to phenol and keten(28)

$$AcOPh \xrightarrow{350\text{-}400^\circ} CH_2{:}CO + PhOH \quad \ldots B^1$$

B^1 scission may occur in competition with other routes as in the breakdown of ethyl acetate(28) where it is a very minor route.

$$AcOEt \begin{cases} \rightarrow AcOH + CH_2{:}CH_2 & \ldots A^1 \\ \rightarrow CH_2{:}CO + EtOH & \ldots B^1 \\ \rightarrow 2MeCHO \end{cases}$$

B^2 type.

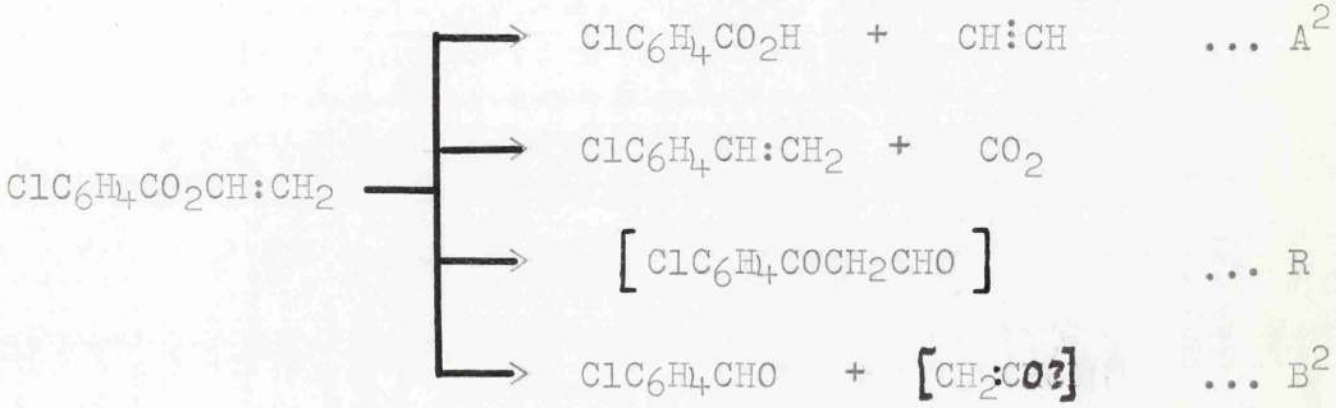
This reaction, giving two aldehydes, is the more common in the absence of β-hydrogen, and where the A^1 scission is possible it is often a minor route.

An early example was reported by Peytral(25), methyl acetate giving two moles of formaldehyde.

$$AcOMe \xrightarrow{1150^\circ} 2CH_2O \quad \ldots B^2$$

Many esters possessing a β-hydrogen have been shown to undergo a minor B^2 scission in a complex pyrolysis at 500°(40).

Reininger and Ritchie(39) found the three isomeric vinyl chlorobenzoates to yield keten(?) and the corresponding chlorobenzaldehyde in a four-route decomposition.



Although only small quantities of the aldehydes were present the reaction is of interest as it was not observed in the pyrolysis of vinyl benzoate(27).

Formally, the reaction is a reversal of the Tishchenko(41) condensation.

$$RCHO + OCHR' \rightarrow RCO_2CH_2R'$$

However, Hurd and Blunck(28) have proposed a radical mechanism on the grounds of the high temperature necessary, but no direct evidence has been recorded.

1.2.4. Elimination Reactions.

C^1 type.

All eliminations of carbon monoxide are considered to be C^1 reactions. Thermal decarbonylation of aldehydes is a well known and general reaction but direct loss from an ester occurs infrequently. At 500° phenyl formate decomposes to phenol by loss of a mole of carbon monoxide(42). A unique example

was reported by Calvin and Lemmon and rigorously established by a tracer technique(77).

$$Me^{14}COCO_2Et \xrightarrow{C^1} CO + CO_2(\text{trace}) + {}^{14}C \text{ by-products}$$

There can be no doubt that the carbon monoxide comes from the ester group and therefore this is a true case of C^1 elimination.

The behavior of acetyl bromide may be compared with that of an ester(43).

$$AcBr \begin{cases} \rightarrow MeBr + CO & \ldots C^1 \\ \rightarrow CH_2{:}CO + HBr & \ldots B^1 \end{cases}$$

Other examples are found in the ethylene and trimethylene oxalates which readily lose carbon monoxide to give the corresponding carbonates(44,45).

Detection of free radicals, by a mercury mirror technique, in the decarbonylation of acetaldehyde and propionaldehyde led to the formulation of a chain mechanism by Swarski and Burton(43), supported by Niclause(46) who suggests initiation by traces of oxygen. The limited information available for direct loss of carbon monoxide from an ester does not indicate any specific mechanism.

$\underline{C^2 \text{ type}}$.

Anschütz observed carbon dioxide to be expelled during the slow distillation of phenyl fumarate(47), phenyl cinnamate and <u>trans</u>-stilbene being identified.

$$PhOCOCH{:}CHCO_2Ph \rightarrow CO_2 + PhCH{:}CHCO_2Ph \rightarrow CO_2 + PhCH{:}CHPh \ldots C^2$$

Comparatively few other instances were known until recent work by Ritchie et al.(26,27,39) showed a number of esters, including vinyl benzoate and chlorobenzoates, in which the A^1 scission was structurally precluded, to decarboxylate. The occurrence of methyl o-toluate in the products from the decomposition of methyl phthalate at 400°(49) is best explained as a loss of a single mole of carbon dioxide.

... C[2]

Methyl esters of α:β-unsaturated aliphatic acids may decarboxylate(48,55) in the region of 500°.

In general this reaction has been observed in molecules having some degree of unsaturation, although one example in a fully saturated compound has been observed by the Author and is discussed later. The association with unsaturation and the elevated temperatures at which the reaction occurs suggest a radical mechanism, but the evidence is inconclusive.

1.2.5. Disproportionation D

Many asymmetrical molecules disproportionate. Some general classes of esters which exhibit this behavior are considered.

When a single carboxyl group of a dibasic acid is esterified the resulting hydrogen ester will readily disproportionate to the acid and the normal ester. Ethyl hydrogen succinate

(50) and phenyl hydrogen sebacate(51) both react thus;

$$2PhOCO(CH_2)_8CO_2H \xrightarrow{\text{distil}} PhOCO(CH_2)_8CO_2Ph + HOCO(CH_2)_8CO_2H \quad \ldots D$$

It is a purely thermal reaction.

A second type of disproportionation occurs in the monoesters of dihydric alcohols(78), equimolar quantities of the diester and the alcohol being the products. At 300 - 350° the monobenzoate of ethylene glycol is smoothly converted to the dibenzoate and ethylene glycol(79).

$$2BzOCH_2CH_2OH \rightarrow BzOCH_2CH_2OBz + HOCH_2CH_2OH \quad \ldots D$$

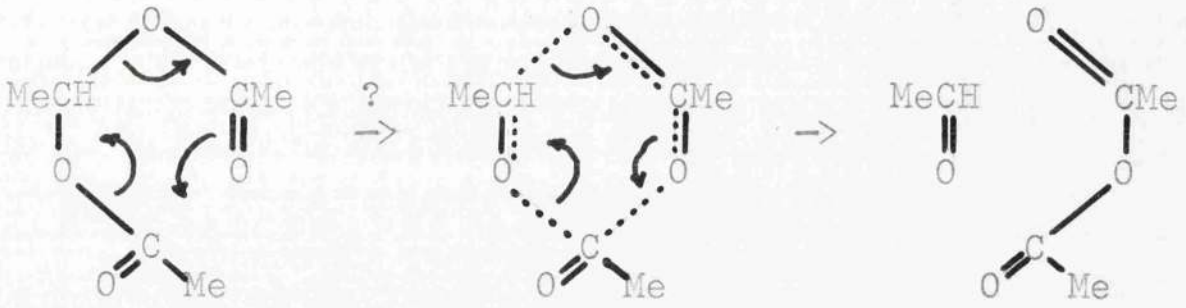
Ethylidene diesters yield acetaldehyde and an acid anhydride by a disproportionation(52). An interesting example was observed in the pyrolysis of ethylene dibenzoate(53). Primary A^1 scission gave vinyl benzoate, which recombined to ethylidene dibenzoate. Secondary decomposition accounted for the unexpectedly large quantities of benzoic anhydride found.

$$CH_2{:}CH(OBz)_2 \rightarrow MeCHO + Bz_2O \quad \ldots D$$

The yields from this reaction are high and the diacetate has been employed in an industrial preparation of acetic anhydride(54)

The mechanism is obscure and it would seem unlikely that a single interpretation would cover all the known cases.

A cyclic transition state has been proposed as an intermediate in the breakdown of the ethylidene diesters(24).



The conditions of minimum electronic displacement and high resonance energy are satisfied.

1.2.6. Rearrangement R.

Thermal rearrangement of esters is a comparatively common reaction. Ethyl maleate isomerises to ethyl fumarate in a complex decomposition at 500°(55), while a similar change is observed during the polycondensation of ethylene glycol and maleic anhydride, the polymer having a trans, fumarate, structure(11).

A number of α:β-unsaturated esters have been reported to rearrange to β-dicarbonyl compounds. It was first observed for isopropenyl acetate by Wislicenus(56) and confirmed recently by Boese and Young(57).

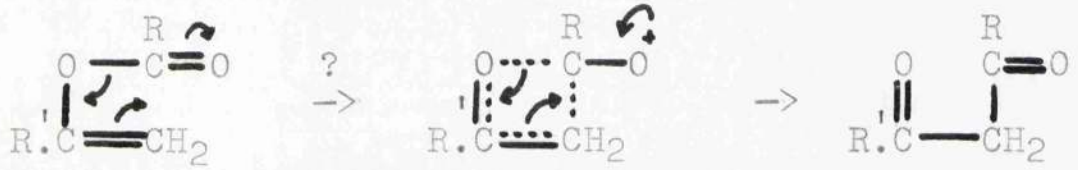
$$AcOCMe{:}CH_2 \rightarrow MeCOCH_2COMe \quad \ldots R$$

Allan, Forman and Ritchie(27) identified acetophenone in the pyrolysate from vinyl benzoate. It was considered that an initial rearrangement would give benzoylacetaldehyde, which was shown to decarbonylate readily.

$$BzOCH{:}CH_2 \xrightarrow{R} PhCOCH_2CHO \rightarrow PhCOMe + CO \quad \ldots C^{1}$$

Another example is the formation of 2-benzoylcyclohexanone from cyclohex-1-enyl benzoate(59).

Young et al.(58) advanced an intramolecular four-membered cyclic transition state for the enol-carboxylate rearrangement.



Where R' is hydrogen the β-ketoaldehyde will decarbonylate.

A Fries type of reaction was found, by Skraup and Beng(60), to occur in phenyl β:β-dimethylacrylate through the agency of heat alone.

The yield of the o-hydroxyketone is small but can be greatly increased by the addition of a trace of hydrogen bromide.

1.2.7. Intra-acyl Scission.

Mackinnon and Ritchie(61) have reported the formation of phenyl formate and an alkyne in the pyrolysis of phenyl acrylate and α-methylacrylate. A primary scission, termed intra-acyl, was proposed.

$$CH_2{:}CRCO_2Ph \xrightarrow{500^{\circ}} CH{:}CR + HCO_2Ph$$

Complete suppression of this route was achieved by the addition of 1 % hydroquinone to the pyrolysand, therefore a free radical mechanism was proposed;

Initiation:

$$CH_2{:}CRCO_2Ph \rightarrow CH_2{:}\dot{C}R + HCO_2Ph$$

Propagation:

i $\quad CH_2{:}\dot{C}R + CH_2{:}CRCO_2Ph \rightarrow CH_2{:}CHR + \cdot CH{:}CRCO_2Ph$

ii $\quad \cdot CH{:}CRCO_2Ph \rightarrow CH{:}CR + \cdot CO_2Ph$

iii $\quad \cdot CO_2Ph + CH_2{:}CRCO_2Ph \rightarrow HCO_2Ph + \cdot CH{:}CRCO_2Ph$

The alkyne and phenyl formate are thus satisfactorily explained.

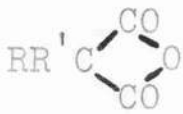
1.3. Pyrolysis of Anhydrides.

Work on the preparation of ketens led to a wide study of the thermal breakdown of acid anhydrides. Wilsmore(63) achieved the first preparation of keten by the action of a hot platinum wire on acetic acid vapour. A dehydration of the acid was suggested and supported by Bamford and Dewar(64), who also recorded a second route.

$$AcOH \xrightarrow{?} \begin{cases} CH_4 + CO_2 \\ CH_2{:}CO + H_2O \end{cases}$$

As the decomposition of acetic anhydride has been shown by Szwarc and Murawski(65) to obey first order kinetics, the sole products being keten and acetic acid, it would seem probable that dehydration of the acid is the initial step in the preparation of keten.

Staudinger(66) deduced, from very extensive investigations, general equations describing the decomposition of substituted malonic anhydrides and those of monobasic acids.



$$RR'C(CO)_2O \rightarrow RR'C{:}CO + CO_2$$

$$(R_2CHCO)_2O \rightarrow R_2C{:}CO + R_2CHCO_2H$$

No acid was reported in the second reaction but later work(65) has shown it to be formed.

A series of monobasic acids, examined by Davidson and Newman(67), were found, contrary to expectations, to undergo thermal dehydration. It was suggested, from analysis of the products, that anhydrides would give two pyrolytic routes.

$$(RCH_2CO)_2O \rightarrow \begin{cases} RCH{:}CO + RCH_2CO_2H \\ (RCH_2)_2O + CO_2 \end{cases}$$

A complex mechanism was employed to account for the ketone formation, a primary condensation of two molecules being involved.

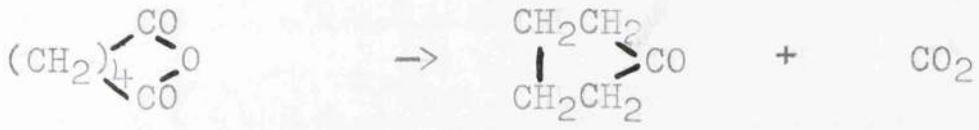
$$2(RCH_2CO)_2O \xrightarrow{?} RCH_2CORCHCO_2COCH_2R + RCH_2CO_2H$$

$$RCH_2CORCHCO_2COCH_2R + (RCH_2CO)_2O \rightarrow RCH_2COCHRCO_2H$$

$$RCH_2COCHRCO_2H \rightarrow (RCH_2)_2CO + CO_2$$

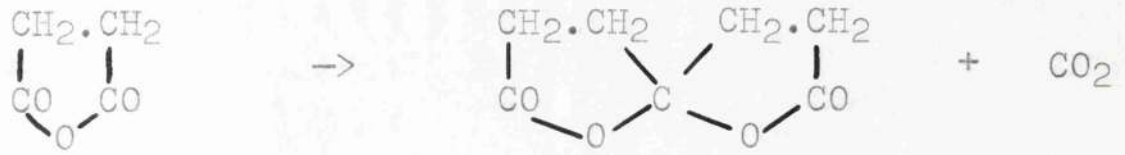
This hypothesis was not substantiated by identification of any of the intermediates and would result in the formation of a large quantity of acid, which was not commented on.

The Blanc Rule(68) states that seven and eight-membered cyclic anhydrides readily lose carbon dioxide yielding stable cyclic ketones. Distillation at atmospheric pressure is sufficient to convert monomeric adipic anhydride to cyclopentanone:

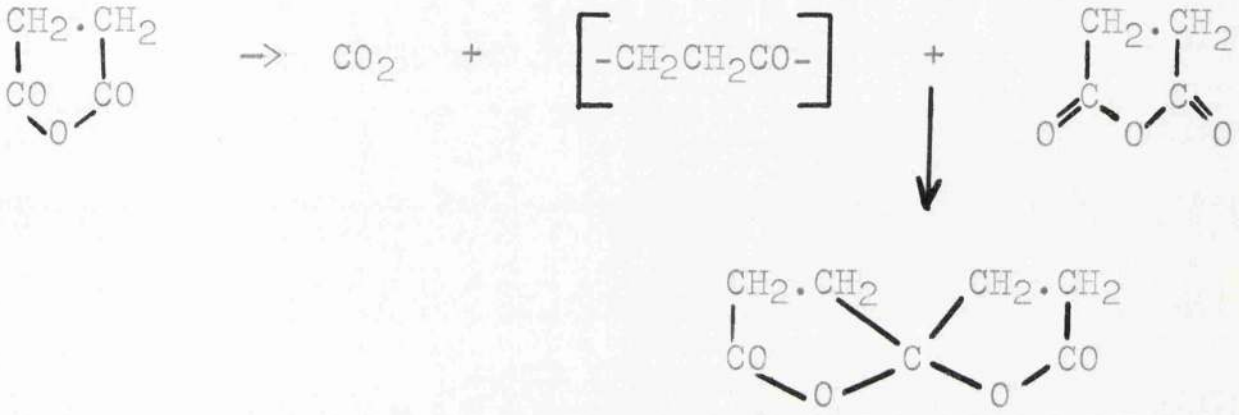


This is comparable with the Dieckmann Reaction(69) for ring closure of ethyl adipate in the presence of sodium ethoxide, a mole of ethanol being eliminated. No mechanism has been established, but, as in the Dieckmann reaction, the α-hydrogen is essential, the α:α'-tetramethyladipic anhydride giving no ketone while the β:β'-tetramethyl compound reacts analogously to the unsubstituted anhydride.

Five-membered ring anhydrides cannot give stable cyclic ketones. Prolonged heating of succinic anhydride at 250 - 280° causes elimination of carbon dioxide and the spiro-dilactone of acetonediacetic acid is present in the residue(71):

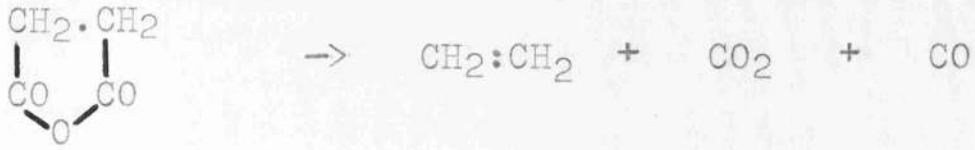


This was confirmed by Hurd and Bennett(72), who regarded the most satisfactory mechanism to be a loss of carbon dioxide from an anhydride molecule to give a diradical which would then add across a >C:O bond of an unchanged molecule.



The evidence available provides no reason to oppose this interpretation.

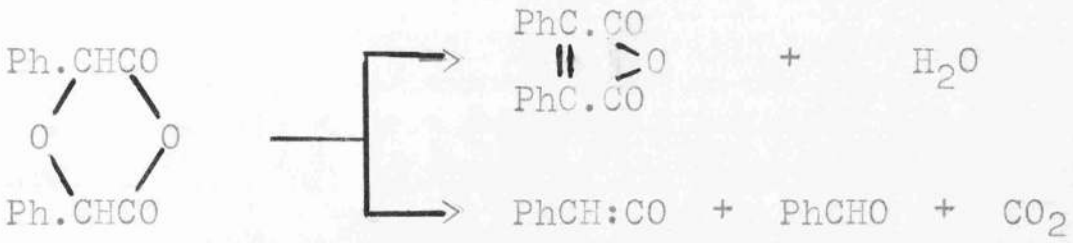
By application of the Principle ofLeast Motion(24), Rice and Murphy(73) predicted the breakdown of a series of compounds related to succinic and maleic anhydrides. In the temperature range 800 - 900° only gaseous products were obtained.



This was in agreement with the postulated route but investigation has now shown this representation to be incomplete.

Anhydrides containing an ether bridge have been found, by Hurd and Glass(74), to undergo a dehydration affecting only the ether bridge and a decomposition of

whole molecule. Loss of a molecule of water from dimandeleic anhydride gives diphenylmaleic anhydride while phenylketen, benzaldehyde and carbon dioxide arise from the second route.



Diglycollic anhydride behaves analogously but the tetraphenyl-substituted compound cannot dehydrate and decomposes by the second route only.

2. DISCUSSION OF RESULTS.

2.1. Pyrolysands.

The thermal breakdown of two series of esters of saturated dibasic acids has been studied; a) the ethyl esters having an available β-hydrogen and b) the methyl esters having no β-hydrogen. Very marked differences were observed both in thermal stability and in the mode of decomposition.

Pyrolysis of a group of related anhydrides was also carried out. Acrylic and α-methylacrylic anhydrides were included, being of interest with regard to previous work on the corresponding methyl(55) and ethyl(48) esters.

In addition to the above it was necessary to examine the behavior of a number of other compounds to elucidate breakdown routes. All pyrolysands are listed in Table 1.

2.2. Qualitative and Semi-quantitative Pyrolyses.

Pyrolyses were carried out in a flow apparatus described in Section 3.1, while reaction conditions and analytical data are tabulated in Section 3.4. The latter were obtained by convential techniques supported by infrared spectroscopy and in the later stages of the work by gas/liquid chromatography.

Quantitative values for breakdown routes are necessarily estimations, the complexity of products preventing accurate measurement. Quantitative application of gas/liquid chromatography was similarly limited but gave useful approximations.

Table 1.

Pyrolysands.

I	Ethyl succinate	XIV	Methyl methylsuccinate
II	Ethyl hydrogen succinate	XV	Methyl propionate
III	Succinic acid	XVI	Methyl allylacetate
IV	Succinic anhydride	XVII	Methyl vinylacetate
V	Ethyl adipate	XVIII	Methyl n-nonoate
VI	Adipic acid	XIX	Methyl n-heptoate
VII	Adipic anhydride	XX	Maleic anhydride
VIII	Ethyl sebacate	XXI	Methylsuccinic anhydride
IX	Sebacic acid	XXII	Acetic anhydride
X	Methyl succinate	XXIII	Acrylic anhydride
XI	Methyl adipate	XXIV	Propiolaldehyde
XII	Methyl glutarate	XXV	α-Methylacrylic anhydride
XIII	Methyl sebacate		

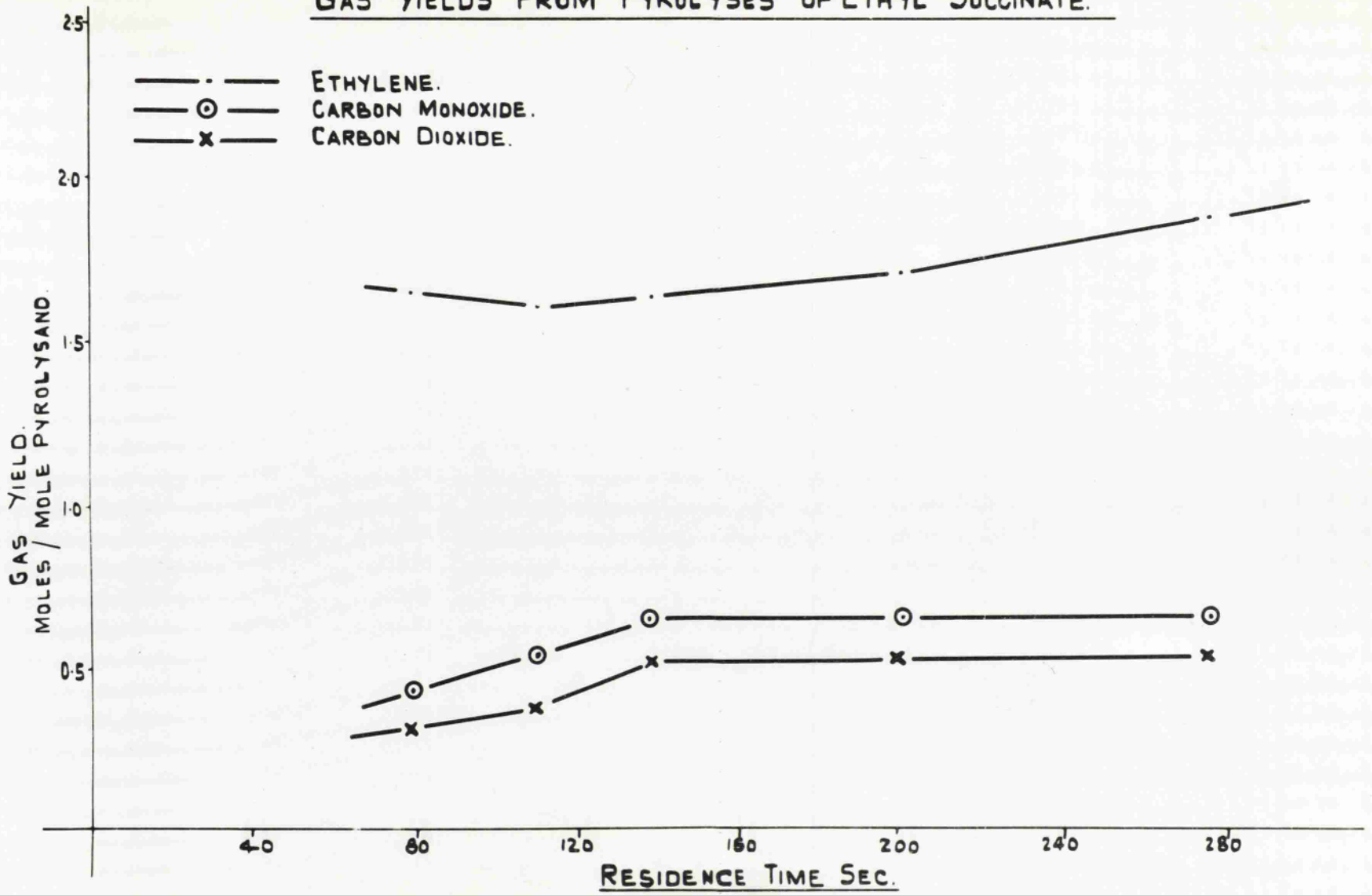

GAS YIELDS FROM PYROLYSES OF ETHYL SUCCINATE.
ETHYLENE.
CARBON MONOXIDE.
CARBON DIOXIDE.
GAS YIELD.
MOLES / MOLE PYROLYSAND.
2·5
2·0
1·5
1·0
0·5
40
80
120
160
200
240
280
RESIDENCE TIME SEC.

FIG. III

2.3. Pyrolysis of Ethyl Esters of Saturated Dibasic Acids.

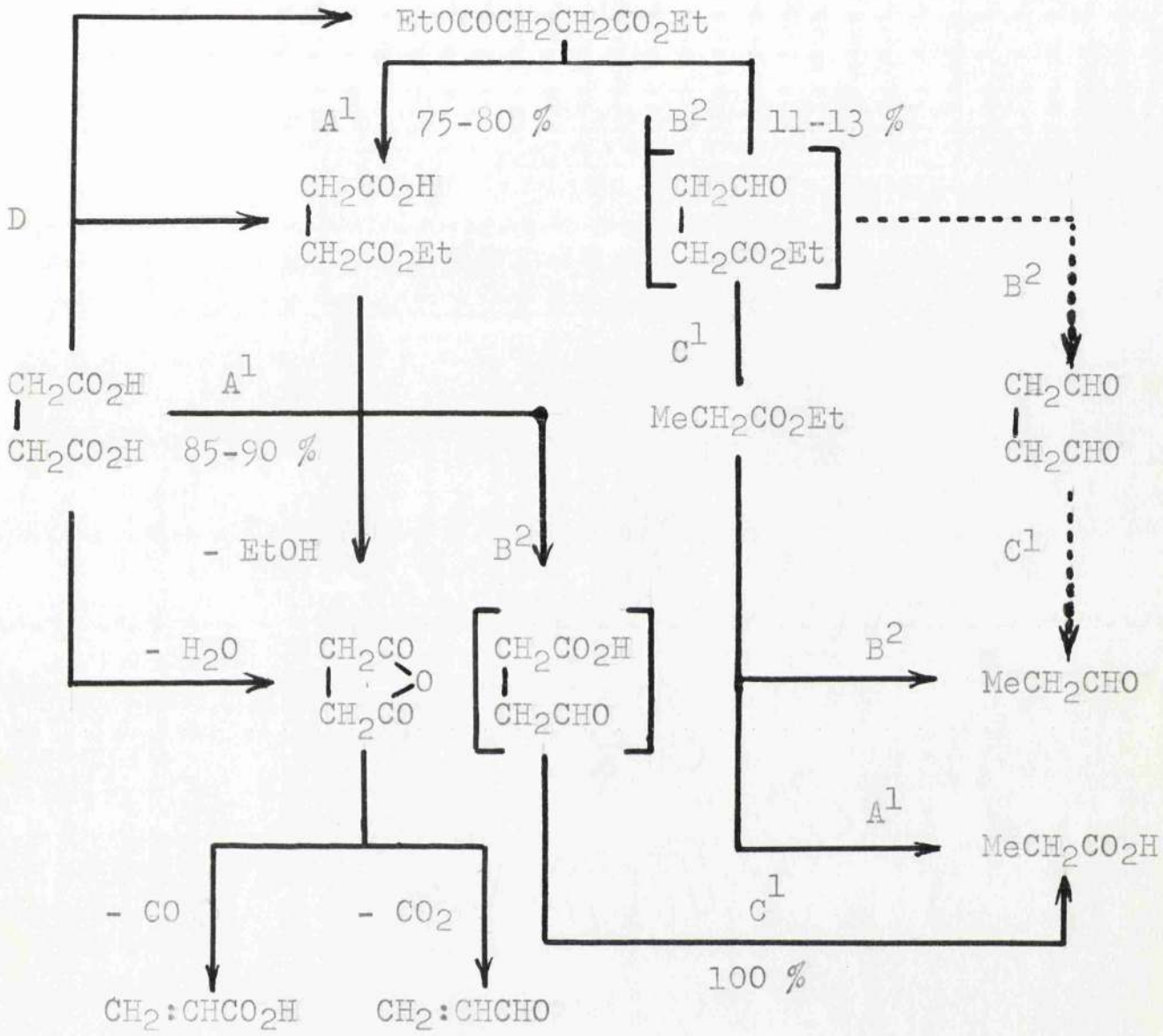
Adipic and sebacic acids are commonly incorporated in polyesters to improve the physical properties of the moulded resin(12). The ethyl esters were chosen as models of the saturated segments and ethyl succinate to represent the points of crosslinking of the polymer chain.

2.3.1. Ethyl Succinate (I).

The total decomposition was 89 - 96 % at 500° and the following gases were produced: ethylene, carbon dioxide and monoxide, ethane and methane, while at high residence times traces of acetylene were also formed. The yields of the principal gaseous products are plotted against residence time, Fig.III, showing an almost linear increase of ethylene over the range 100 - 275 seconds, which suggests a unimolecular reaction. The quantities of carbon monoxide and dioxide approach a constant value and the molar ratio, table 2, remains approximately constant. Although the formation of these gases, in the measured ratio, *via* a single route would explain the results, deviations caused by minor routes cannot be accurately determined.

As would be expected from the presence of the β-hydrogen, A^1 scission is the major route, evidenced by the large yield of ethylene. Identification of succinic acid(III) and ethyl hydrogen succinate(II) suggests that rupture of the two alkyl-

Decomposition of ethyl succinate at 500°



For simplicity the following products have been omitted;

A^1 scissions - ethylene

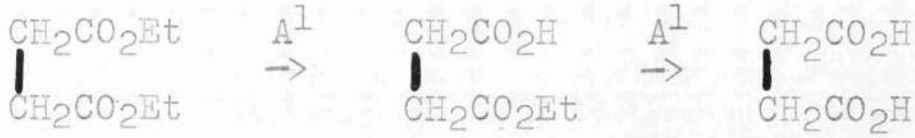
B^2 scissions - acetaldehyde

C^1 scissions - carbon monoxide

Further decomposition of end products occurs by known routes.

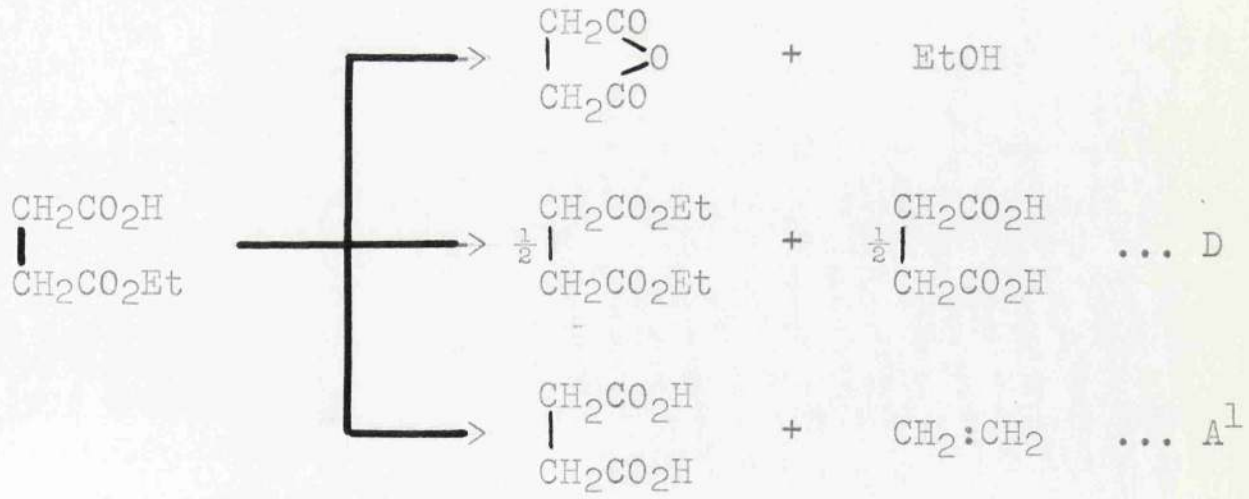
Unidentified compounds are surrounded by square brackets and dotted lines indicate tentative routes.

oxygen bonds occurs consecutively, thus;



Large quantities of succinic anhydride, water and minor amounts of ethanol were also present. Dehydration of the acid(80) and YIELDS most of the anhydride but a minor ring closure of ethyl hydrogen succinate(81) would give the latter by elimination of ethanol.

Pyrolysis of (II) confirmed the A^1 scission and the ring closure, while isolation of a trace of ethyl succinate established the disproportionation which is known to occur at lower temperatures(50).



A difficulty exists in differentiating the A^1 scission of the monoester and the $D/2A^1$ reaction, succinic acid being the end product of both. Reference to the behavior of ethylene glycol monobenzoate provides a useful comparison. It has been shown by Iengar and Ritchie(79) to disproportionate

smoothly at 375°, while at 500° olefin elimination predominates. Ethyl propionate, formed from (I) by a B^2/C^1 scission, was not obtained from (II), which is consistent with a minor disproportionation since acid decarboxylation is known not to occur readily(82,83).

$$\begin{matrix} CH_2CO_2H \\ | \\ CH_2CO_2Et \end{matrix} \quad \not\rightarrow \quad MeCH_2CO_2Et + CO_2$$

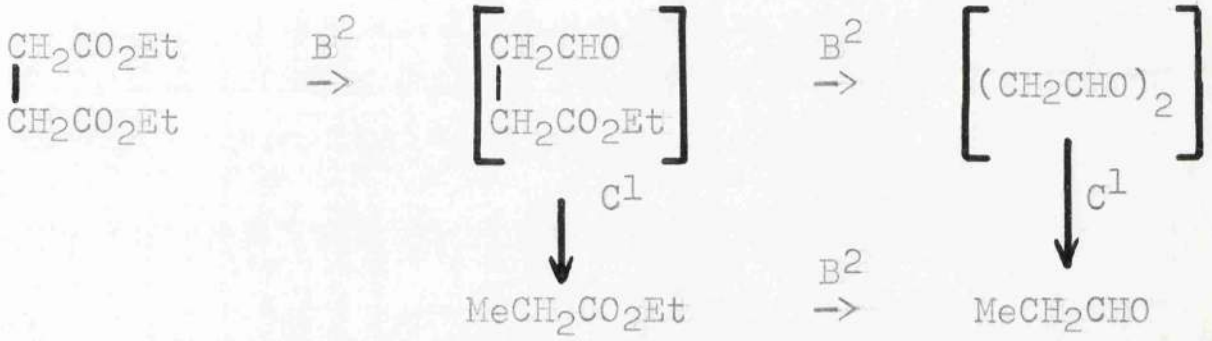
Oppenheim and Precht(84) showed ethyl acetate to eliminate ethylene at a lower temperature than that required for decarboxylation of acetic acid. Further support for the preference of A^1 scission over disproportionation is found in the molar ratios of carbon monoxide to dioxide, Table 2, which in the pyrolyses of (I) are 1.14 - 1.40 over a wide range of residence times, while from the hydrogen ester the figures are 2.1 and 3.0. The higher figures in the second case are inconsistent with a major disproportionation.

Table 2.

Pyrolysand	I	I	I	I	I	II	II	III	IV	IV
Run No.	1	2	3	4	5	6	7	8	9	39
Mole Ratio $\frac{CO}{CO_2}$	1.34	1.3	1.14	1.32	1.4	2.13	3.0	1.18	2.15	4.7

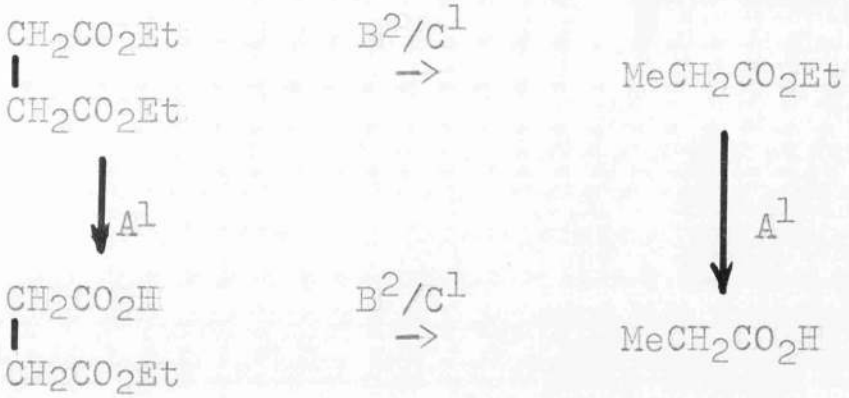
Two sites exist for acyl-oxygen scission which may occur at both or B^2 and A^1 scissions at different ester groups in the same molecule. Acetaldehyde and propionaldehyde were the only

carbonyl products, which is not surprising from the known ease of decarbonylation(85,86). These are regarded as confirming a double B^2 scission followed by loss of carbon monoxide, while a B^2/C^1 sequence accounts for ethyl propionate.



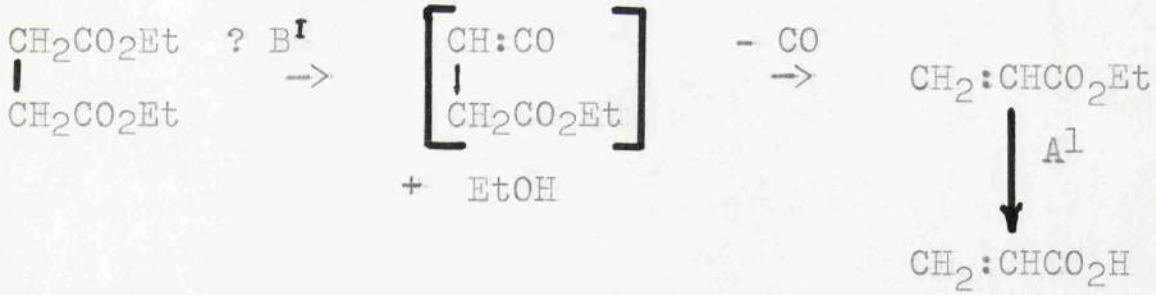
It is seen that propionaldehyde can arise without the necessary formation of the dialdehyde. As ethyl β-formyl-propionate, the primary product of acyl-oxygen scission, would lose carbon monoxide in preference to decomposition of the ester group, it must be concluded that only traces of succinodialdehyde would be formed, and it is unlikely to survive pyrolysis conditions in detectable quantity.

Confirmation of rupture of alkyl-oxygen and acyl-oxygen bonds in the same molecule was obtained by the identification of propionic acid in the pyrolysates from (I) and(II). Only one route is possible for the latter, namely the B^2/C^1 reaction, but elimination of ethylene from ethyl propionate provides a second route in the breakdown of ethyl succinate. The unstable intermediates, β-formylpropionic acid and ethyl β-formyl-propionate, could not be isolated.



Decarboxylation of ethyl hydrogen succinate must be discounted from the previous discussion.

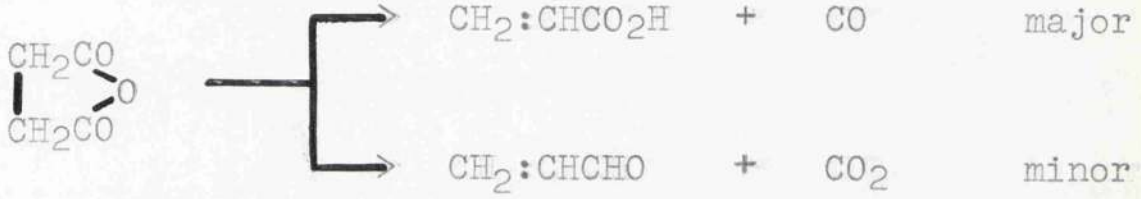
One important product, acrylic acid, remains to be accounted for. It is possible to formulate a route involving B^1 scission, which has the support of the production of ethanol and the known decomposition of keten(64):



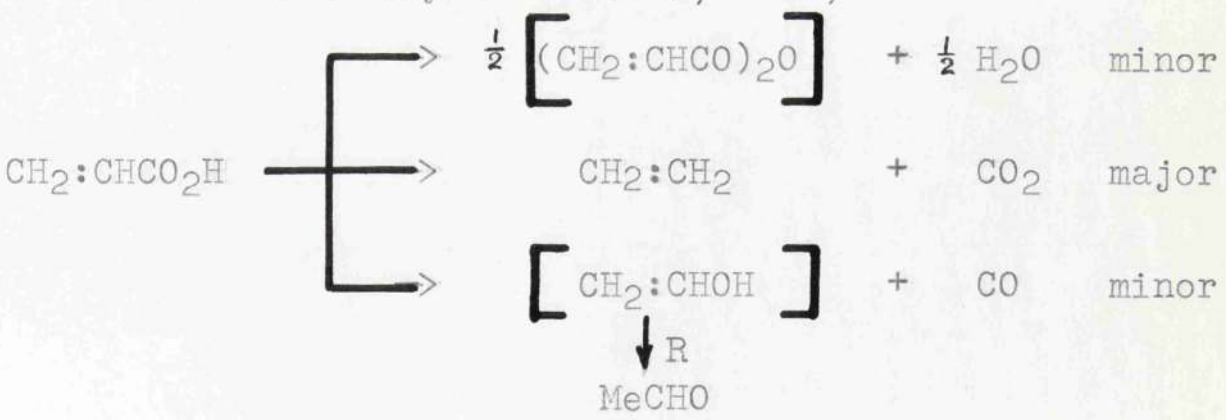
Ethyl acrylate could not be detected but is known to be unstable at 500°(48). 15 % ester decarboxylation was shown to occur, yielding n-but-1-ene, but in the present examination this gas was not formed. Ethyl acrylate, therefore, cannot be an intermediate and the above scheme is unsatisfactory.

An attempt to resolve the problem by pyrolysING secondary products from (I) revealed the interesting fact that succinic acid and anhydride gave major quantities of

acrylic acid. The primary reaction of the acid is an exclusive dehydration. The decomposition of the anhydride is discussed in detail in Section 2.4, but the results may be stated here. Pyrolysis occurs by two routes to acrylic acid and to acrolein, with elimination of a mole of carbon monoxide and dioxide respectively.



Acrolein was not detected in the ethyl succinate pyrolysate, the result of the minor nature of the route and secondary breakdown to ethylene and carbon monoxide(48). It has also been shown that acrylic acid undergoes major decarboxylation and minor C^1 scission and dehydration(48), thus;



The anhydride is unstable but the known breakdown products (Section 2.4) were confirmed. This is the most probable source of acetylene but pyrolysis of ethylene cannot be disregarded. The latter reaction is complex, giving (in addition to acetylene) hydrogen, methane and ethane, but these gases would have no significant effect on the analysis.

At 500° ethyl succinate decomposes by two routes, a major A^1 scission and a minor B^2 scission. In a single molecule the ester groups can undergo one or both types of breakdown, indicating that there is no significant interaction of the functional groups. The total decomposition, including secondary reactions, is given(page 25[a]) with approximate quantitative figures.

2.3.2. Ethyl Adipate (V).

4 - 7 % of this ester survived pyrolysis at 500°, residence times varying from 44 to 214 seconds. The gaseous pyrolysate contained ethylene, carbon monoxide and dioxide, methane and traces of n-butane and n-but-1-ene, while at the highest residence times some acetylene was also found.

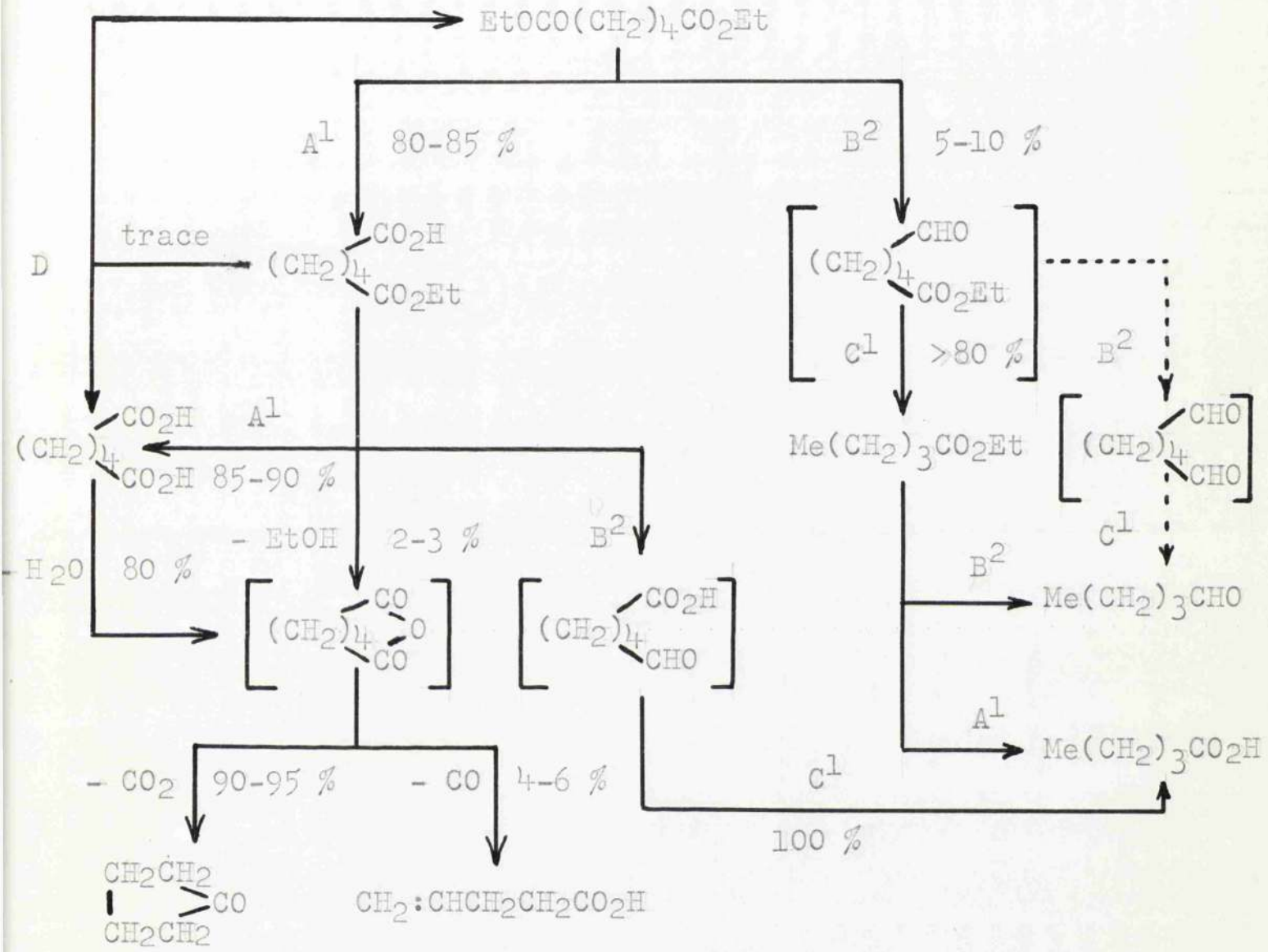
A high proportion of ethylene in the gases suggested a major A^1 scission, which was confirmed by identification of adipic acid and ethyl hydrogen adipate, the ruptures being consecutive as in the decomposition of ethyl succinate.

$$(CH_2)_4(CO_2Et)_2 \xrightarrow{A^1} (CH_2)_4(CO_2H)(CO_2Et) \xrightarrow{A^1} (CH_2)_4(CO_2H)_2$$

The olefin indicated that approximately 87 % of the breakdown occured by this route but the hydrogen ester and acid were considerably deficient.

The structural similarity to the succinate suggests

Decomposition of ethyl adipate at 500°.



Omitted from the scheme are products from;

A^1 scission - ethylene

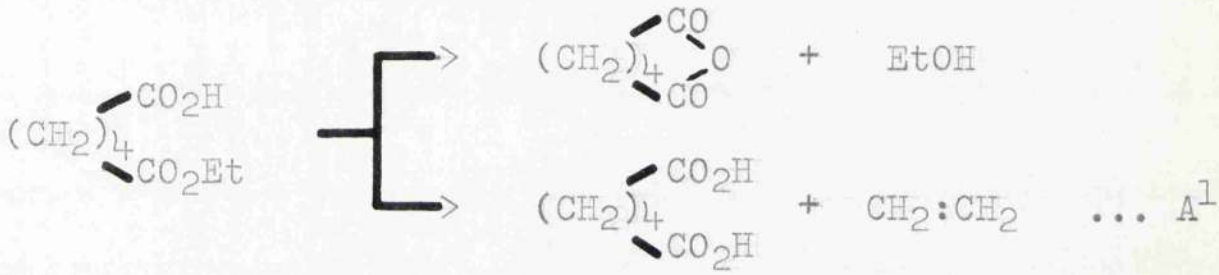
B^2 scission - acetaldehyde

C^1 scission - carbon monoxide

Further decomposition of end products occurs by known routes.

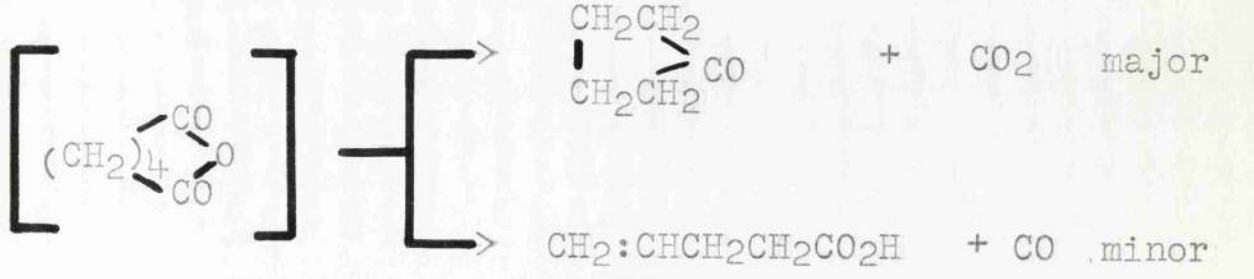
Unidentified compounds are surrounded by square brackets and dotted lines indicate tentative routes.

that the decomposition of ethyl hydrogen adipate will be analogous to that of the lower homologue. A disproportionation has been established at lower temperatures(50) but would be of minor importance at 500° yielding no unexpected products. It will not be further considered. Ethylene elimination will predominate but the formation of a small quantity of ethanol is accountable by a minor cyclisation to the anhydride.



Further indication of the formation of anhydride was found in the presence of water in the pyrolysate from ethyl adipate, but testing with the sensitive colour reaction(88) failed to reveal even traces.

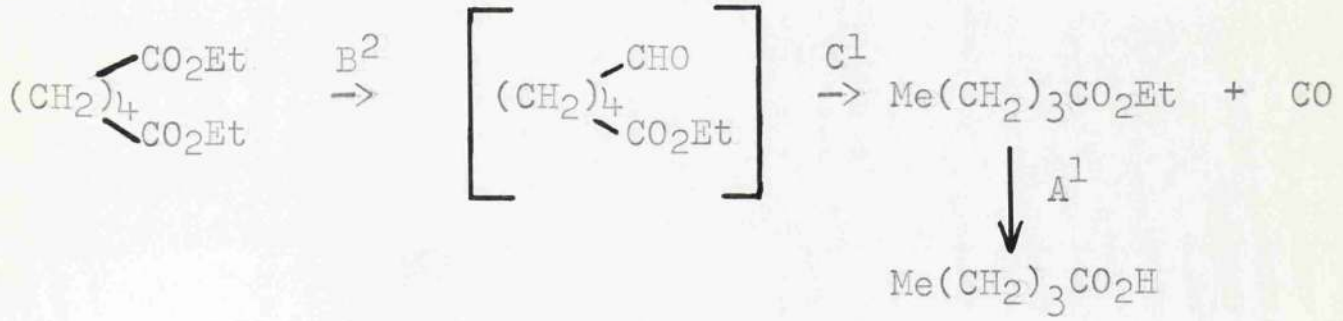
Monomeric adipic anhydride decomposes, almost quantitatively, to cyclopentanone at 250 - 280°(68). Examination in the flow system at 500° showed greater than 95 % decomposition, the results being attributable to two routes(Section 2.4.)



Ethyl adipate gave cyclopentanone, in quantity, and a trace

of allylacetic acid, verifying the routes. The total decomposition of the anhydride under pyrolysis conditions was tested by distillation of the acid, known to be stable at its boiling point(89), through a horizontal furnace at 500°. Water and cyclopentanone were the main constituents of the pyrolysate but the anhydride was not present in detectable quantity. A possible explanation is that the anhydride formed at 500° is in a more active state than the pure compound used as a pyrolysand and is less stable. However, from the evidence, it must be assumed that in the pyrolysis of ethyl adipate the anhydride decomposes at the same rate as it is formed.

Acyl-oxygen scission was indicated by significant quantities of acetaldehyde. The aldehydo-ester, primary product of a single scission, was not isolated but the best explanation of ethyl n-valerate is a B^2/C^1 reaction, thus;

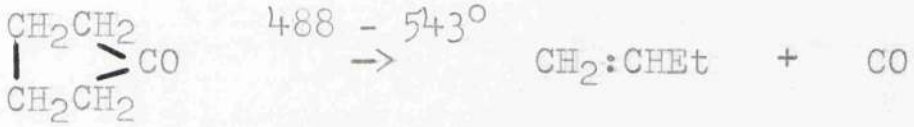


The identified n-valeric acid arises *via* elimination of a second mole of ethylene.

Theoretically, adipic dialdehyde may be produced by successive B^2 scissions, but for the same considerations given for ethyl succinate, decarbonylation of ethyl 4-formyl-n-

valerate would occur with considerably greater ease than elimination of acetaldehyde. For this reason a B^2 scission of ethyl n-valerate is regarded as the principal source of n-valeraldehyde.

Methane, n-butane and n-but-1-ene remain to be accounted for. The saturated gases are expected products from decarbonylation of acetaldehyde(85) and n-valeraldehyde respectively, while n-but-1-ene has been shown to be a breakdown product of cyclopentanone(90).



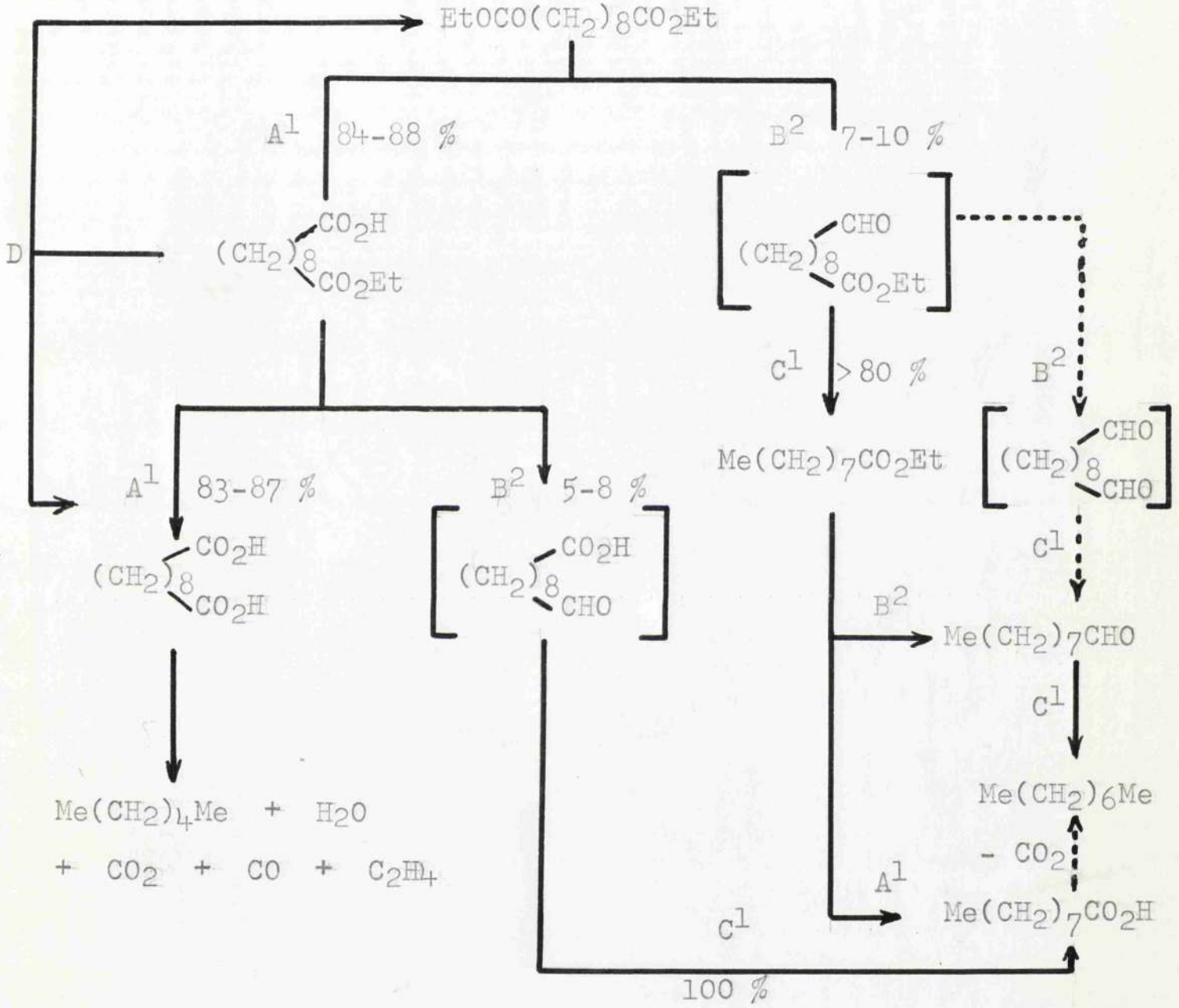
The source of acetylene cannot be stated with certainty. It is only formed at high residence times, thus dehydrogenation of ethylene is possible(87) and appears the most acceptable explanation.

Primary decomposition of ethyl adipate can occur by A^1 or B^2 scission and a molecule may undergo one or both at different ester groups. A representation of these and the secondary breakdown is given on page 31[a].

2.3.3. Ethyl Sebacate (VIII).

At 500° the total decomposition, 96 - 98 %, was rather greater than for the lower homologues and larger quantities of gas were produced. The principal constituent of the latter

Decomposition of ethyl sebacate at 500°



Omitted from the scheme are the products from;

A^1 scission - ethylene

B^2 scission - acetaldehyde

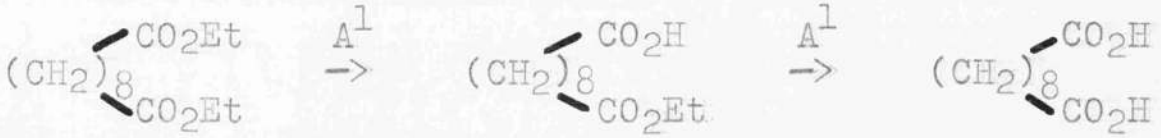
C^1 scission - carbon monoxide

Complex minor reactions are not elucidated.

Square brackets surround unidentified compounds and dotted lines indicate tentative routes.

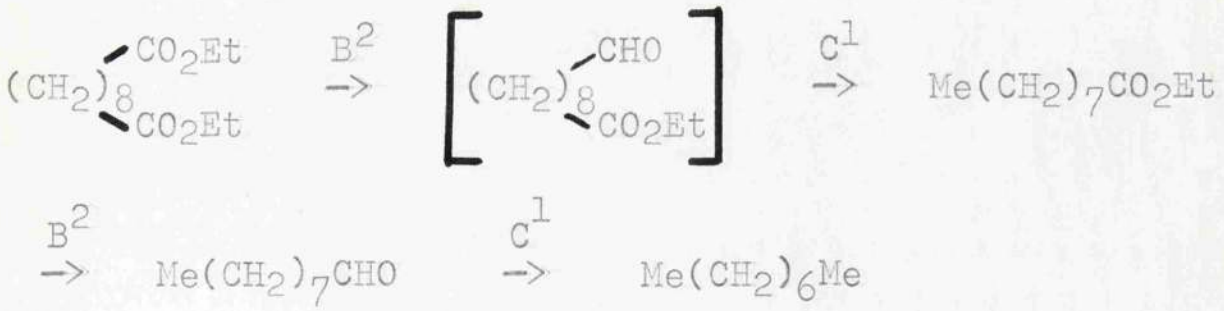
was ethylene with smaller amounts of carbon monoxide, dioxide, methane and acetylene, present as a trace increasing to 1.4 % at a residence time of 205 seconds.

Sebacic acid, in quantity, and traces of ethyl hydrogen sebacate established major consecutive A^1 scissions.



Disproportionation of the hydrogen ester(91) is discounted on the grounds that strong preference is shown for A^1 scission at high temperatures(79) and ethyl sebacate is unstable at the pyrolysis temperature. Absence of ethanol excluded ring closure.

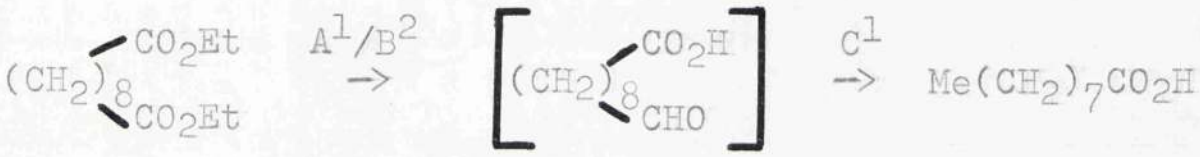
Acyl-oxygen scission is confirmed by formation of acetaldehyde, pelargonaldehyde and n-octane, thus;



The aldehydo-ester, which would be expected to be unstable, was not identified, while an ester corresponding to ethyl pelargonate was detected but not rigorously characterised. The arguments stated in the discussion on the breakdown of ethyl succinate and adipate, favouring a B^2/C^1 sequence before

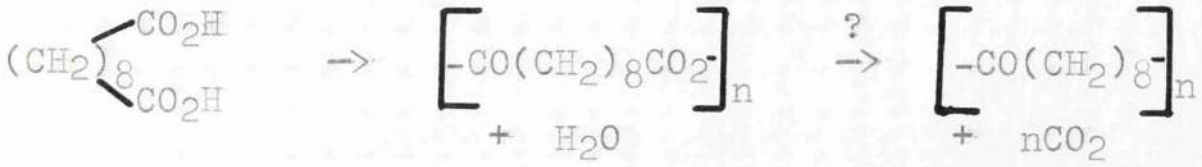
decomposition of the second ester group, apply here, the formation of a dialdehyde being, therefore, improbable. It is, however, included in the scheme(page 34[a]) as a tentative, unconfirmed route.

A carboxyl group is more stable than an ester containing a β-hydrogen(82,83) therefore decarboxylation of ethyl hydrogen sebacate is not expected. Formation of pelargonic acid is probably <u>via</u> the aldehydo-acid from a A^1/B^2 reaction.



Loss of carbon dioxide from pelargonic acid may contribute a trace to the yield of <u>n</u>-octane but the reaction is of minor significance.

The monomeric anhydride of sebacic acid is formed with great difficulty(92) but water in the ethyl sebacate pyrolysate suggests a thermal dehydration. An attempted pyrolysis of the acid, by distillation through an horizontal furnace at 500°, gave water, equivalent to almost total dehydration, the reaction occurring mainly at the boiling point, leaving a dark, tarry residue. The gas yield per mole of acid was 1.1 mole carbon dioxide, 0.17 mole carbon monoxide and 0.17 mole ethylene. A possible explanation is the formation, in the liquid phase, of a polymeric anhydride which then loses carbon monoxide to give a polymeric ketone, thus;



It has been shown that the liquid phase pyrolysis of bis-2-ethyl- (CYCLOHEXYL Λ) sebacate(22), at 350°, gives a polymeric ketone, in the presence of metallic powders, although under the same conditions the acid does not. Tests for anhydride were negative as with the pyrolysate from the ethyl ester. Of greater interest is the formation of ethylene, carbon monoxide and a trace of n-hexane. These were also products from the ester and are attributed to a complex breakdown of monomeric anhydride formed in the vapour phase, the dilution effect preventing polycondensation.

The relatively higher yield of acetylene from the sebacate cannot be accounted for by any of the considered secondary decompositions. Ethylene dehydrogenation would appear to be the source, the higher molar concentration, arising from the higher molecular weight of the acid residue, giving the greater yield.

The decomposition of ethyl sebacate is analogous to that of the lower homologues studied, A^1 and B^2 scissions occurring independently at either ester group. The breakdown scheme is given on page 34[a].

2.4. Pyrolysis of Methyl Esters of Saturated Dibasic Acids.

The methyl esters of succinic, adipic and sebacic acids give a useful comparison with the ethyl esters showing the effect of absence of β-hydrogen. Information, required, of the effects of a side-chain substituent and an odd number of methylene groups has been obtained by examination of the decomposition of methyl methylsuccinate and glutarate respectively.

2.4.1. General Pyrolytic Reactions of Methyl Esters.

Relatively little work has been carried out on the breakdown of methyl esters but alkyl-oxygen, $A^{o}(25)$ and acyl-oxygen scissions, $B^{1}(48)$ and $B^{2}(93)$, have been observed, the last being the most common.

The esters studied were found to be relatively stable, not more than 31 % decomposing at residence times up to 200 seconds. Each yielded a gaseous pyrolysate containing carbon dioxide, monoxide, ethylene, methane and hydrogen together with traces of acetylene(methylacetylene $^{\neq}$) and propene. Other products common to all reactions were methyl acetate, n-butyrate and acrylate(α-methylacrylate and crotonate $^{\neq}$), methanol, methyl formate and formaldehyde. Because of this similarity each product is considered separately rather than discussing individual esters.

$^{\neq}$ corresponding products from methyl methylsuccinate.

2.4.2. Formation of α:β-Unsaturated Esters.

Methyl acrylate(α-methylacrylate and crotonate ≠) was the surprising and interesting principal product from all pyrolysands. The routes whereby it may be formed are considered.

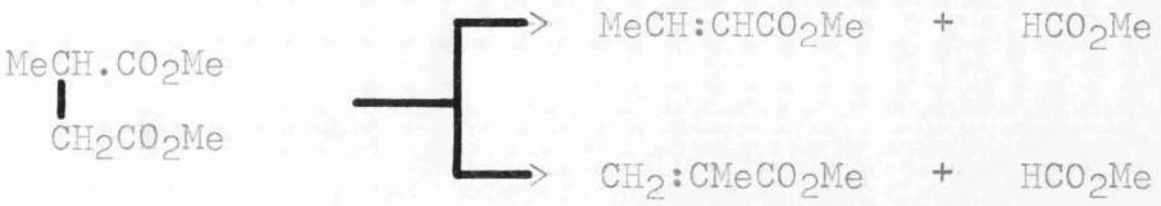
The most obvious route which must be considered is the B^1 scission which by elimination of methanol gives an unsaturated molecule. It has been detected in the pyrolysis of methyl phenylacetate by Engler and Low(93). Applied to the decomposition of methyl succinate and methylsuccinate a keten will be formed, thus;

$$\begin{matrix} CH_2CO_2Me \\ | \\ CH_2CO_2Me \end{matrix} \xrightarrow{?\ B^1} \left[\begin{matrix} CH{:}CO \\ | \\ CH_2CO_2Me \end{matrix}\right] \rightarrow CH_2{:}CHCO_2Me$$

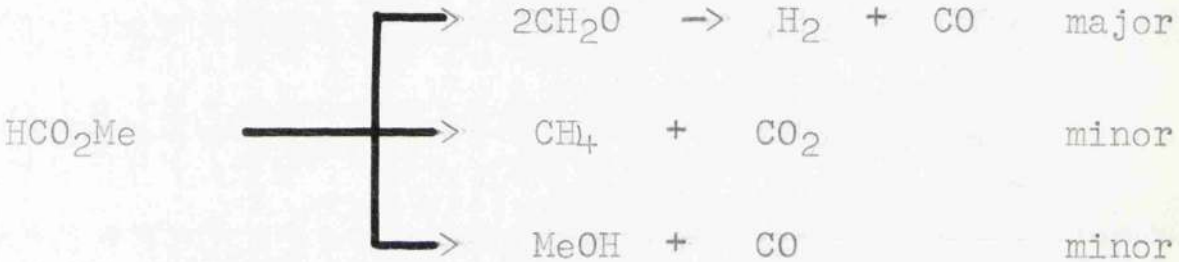
Loss of carbon monoxide is in accordance with the known, major breakdown of keten(64), methyl substitution having no effect other than to stabilise the keten. Against this interpretation are the facts that no ketens were detected and, more important, the quantity of methanol was considerably less than the unsaturated ester in all cases. Secondary decomposition cannot satisfactorily account for this deficiency. Methanol yields formaldehyde, carbon monoxide and hydrogen at 500°(98) but the extent of breakdown is very small. The inapplicability to the higher homologues conclusively disproves this route.

A more consistent explanation can be formulated if a primary scission, giving the unsaturated ester, is assumed,

methyl formate being the other product.



Methyl formate is deficient but has been shown to decompose by three routes(55,94) only 40 % surviving at 500°



All the products shown were identified, the formaldehyde being, generally, greater than expected. A previous example of elimination of a formate from an ester was recorded by Mackinnon and Ritchie(31).

Phenyl acrylate and α-methylacrylate behave in this way, both being similar to methyl esters in that they possess no β-hydrogen.

The main weakness of the above argument is that it cannot hold for esters having more than two methylene groups. The products of a splitting-off of methyl formate would be esters having terminal unsaturation, thus;

$$(CH_2)_n\begin{matrix}CO_2Me\\CO_2Me\end{matrix} \xrightarrow{?} \left[CH_2{:}CH(CH_2)_{n-2}CO_2Me\right] + HCO_2Me$$

However, methyl vinylacetate and allylacetate, which should be formed from the glutarate and adipate respectively, were not present in the pyrolysates. A separate pyrolysis of methyl vinylacetate and of methyl allylacetate showed both to survive to more than 50 % and neither to yield methyl acrylate. It is not possible that these compounds could have escaped detection.

The possibility of a simple carbon-chain rupture exists, comparable to cracking of a paraffin to ethylene and a lower homologue(95).

$$(CH_2)_n\begin{matrix}CO_2Me\\CO_2Me\end{matrix} \xrightarrow{?} CH_2{:}CHCO_2Me + Me(CH_2)_{n-3}CO_2Me$$

Methyl acetate and methyl propionate were obtained from the glutarate and adipate respectively, in slightly smaller quantity than the acrylate, while n-heptaldehyde was taken to confirm scission of the β:γ-carbon bond of methyl sebacate. A precedent exists in the decomposition of esters of long chain fatty acids, phenyl laurate, stearate and palmitate(96).

$$RCH_2CH_2CO_2Ph \rightarrow RH + CH_2{:}CHCO_2Ph$$

The acrylate was accompanied by phenol, acetylene and carbon monoxide from secondary decomposition, phenyl formate being

unstable.

$$CH_2{:}CHCO_2Ph \rightarrow CH{:}CH + HCO_2Ph \rightarrow CO + PhOH$$

In the present work this reaction has been confirmed for the straight chain methyl esters, methyl n-heptoate and n-nonoate, as a major route in the complex breakdown.

Scission of the β:γ-bond of any of the esters under examination can account for the formation of an α:β-unsaturated ester. Methyl succinate and methylsuccinate are exceptional in that the corresponding saturated product, methyl formate, is relatively less stable than the higher homologues.

It remains to account for methyl formate in the pyrolysates from the esters having more than two methylene groups. Although the quantities were similar to those from the succinate, the secondary decomposition products were appreciably less. Pyrolyses of methyl propionate, pelargonate (n-nonoate), n-heptoate, vinylacetate and allylacetate all yielded small amounts of methyl formate, thus the most satisfactory explanation is secondary decomposition of simple esters formed in the course of pyrolysis.

One exception to the rule of scission of the β:γ-bond is found in the breakdown of methyl methylsuccinate. Although the crotonate and α-methylacrylate are formed, as previously stated, a small quantity of methyl acrylate was also identified, indicating a rupture of the α:β-bond, thus;

$$\begin{array}{l} MeCH.CO_2Me \\ | \\ CH_2CO_2Me \end{array} \rightarrow CH_2{:}CHCO_2Me + MeCO_2Me$$

This unusual result may be regarded as consistent with the general reaction, since the structure does allow the formation of an α:β-unsaturated ester in this way whereas it is not possible in the absence of an α-substituent.

The generalisation may be made that methyl esters of saturated dibasic acids will undergo thermal decomposition such that an α:β-unsaturated and a saturated ester will be formed.

2.4.3. Acyl-oxygen Scission B^2

Formaldehyde is not necessarily indicative of acyl-oxygen scission; as has been shown, it may be formed by decomposition of methyl formate, but the quantities were generally greater than could be accounted for in this way.

The aldehydo-ester, product of a single B^2 scission, did not in any pyrolysis survive. Ready decarbonylation is probable from the known reactions of simple aldehydes(85,86).

$$(CH_2)_n\begin{array}{l}CO_2Me \\ CO_2Me\end{array} \xrightarrow{B^2} \left[(CH_2)_n\begin{array}{l}CHO \\ CO_2Me\end{array}\right] \xrightarrow{C^1} Me(CH_2)_{n-1}CO_2Me + CO$$

Methyl succinate, methylsuccinate and glutarate gave the saturated esters corresponding to this reaction, namely

methyl propionate, n-butyrate and isobutyrate, and n-butyrate respectively. No esters attributable to the B^2/C^1 reaction of the adipate or sebacate were identified.

The high stability of the methyl ester group indicates that the aldehydo-ester will lose carbon monoxide in preference to any reaction of the second functional group, thus no dialdehydes will be formed. The simple esters arising *via* a B^2/C^1 reaction of methyl succinate, methylsuccinate and glutarate, underwent B^2 scission which was confirmed by identification of the appropiate aldehydes, propionaldehyde, isobutyraldehyde and n-butyraldehyde.

The pyrolysates from methyl adipate and sebacate did not contain the aldehydes expected from a $2B^2/C^1$ sequence but it may be inferred from the normal paraffins found that B^2/C^1 scissions occured at both ester groups.

$$(CH_2)_n\begin{matrix}CO_2Me\\CO_2Me\end{matrix} \xrightarrow{B^2/C^1} Me(CH_2)_{n-1}CO_2Me \xrightarrow{B^2/C^1} Me(CH_2)_{n-2}Me$$

The adipate gave n-butane and the sebacate n-octane. Despite the non-identification of the intermediate esters, the above route seems the most acceptable.

2.4.4. Formation of Methyl Acetate.

The presence of methyl acetate in the products from methyl glutarate and methylsuccinate is explained by the formation of α:β-unsaturated esters, but the smaller but

nevertheless significant quantities obtained from the other esters cannot be associated with the unsaturated products. Carbon-chain scission can be invoked as a possible explanation, thus;

$$(CH_2)_n\begin{matrix}CO_2Me\\CO_2Me\end{matrix} \xrightarrow{?} AcOMe + \left[CH_2{:}CH(CH_2)_{n-3}CO_2Me\right]$$

No unsaturated esters were found which would support this; also, in the case of the succinate, the energy barrier would be high, as the residual fragment could not rearrange to a stable molecule.

A tentative route to methyl acetate, applicable to all pyrolyses, can be formulated by assumption of a free radical mechanism. Mackinnon and Ritchie(31) proposed a $\cdot CO_2Ph$ radical in the formation of phenyl formate from phenyl acrylate. By analogy it is reasonable to suggest that $\cdot CO_2Me$ takes part in the production of methyl formate from the methyl esters. Loss of carbon dioxide gives the more stable methyl radical, which could combine with an unchanged $\cdot CO_2Me$, thus;

$$\cdot CO_2Me \rightarrow Me\cdot + CO_2$$

$$\cdot CO_2Me + Me\cdot \rightarrow MeCO_2Me$$

This would be general for all methyl esters which give methyl formate. It is favoured by the formation of methyl acetate in the pyrolysis of methyl propionate, n-nonoate and n-heptoate. The validity of the mechanism depends on the truth of the

initial assumption which is discussed in detail in Section 2.5.

2.4.5. Decarboxylation.

Known examples of ester decarboxylation(26,27,48) have been observed in molecules having some unsaturated or benzenoid character. Evolution of carbon dioxide, reported by Korshak and Rogozhin(97), during the polycondensation of ethylene glycol with a dibasic acid, of general formula $HOCO(CH_2)_nCO_2H$, is classed as C^2 scission since the acids do not decompose under the same conditions.

The formation of methyl n-butyrate from methyl succinate is interesting as an instance of decarboxylation of a completely saturated, simple ester.

$$\begin{matrix} CH_2CO_2Me \\ | \\ CH_2CO_2Me \end{matrix} \xrightarrow{C^2} Me(CH_2)_2CO_2Me + CO_2$$

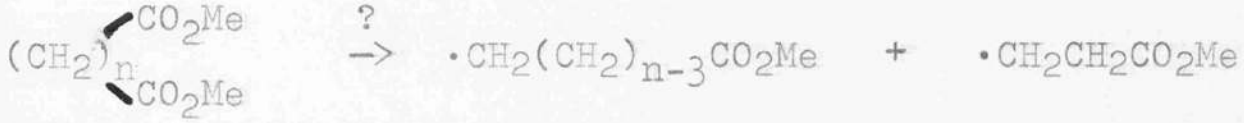
It cannot be stated with certainty whether direct loss of carbon dioxide occurs or if methyl n-butyrate results from a complex reaction. The latter contention is supported by the presence of methyl n-butyrate in the pyrolysates from the homologues, but no evidence for decarboxylation was found.

2.4.6. Formation of Methyl n-Butyrate from Methyl Adipate and Sebacate.

Methyl n-butyrate, formed from all the esters under consideration, is unexplained in the case of the adipate and sebacate. The requirements for carbon-chain scission,

corresponding unsaturated esters, are not fulfilled by the findings.

If two radicals are produced by the established scission of the β:γ-bond then condensation with a methyl radical gives a feasible explanation of the butyrate, thus;



$$(CH_2)_n(CO_2Me)_2 \xrightarrow{?} \cdot CH_2(CH_2)_{n-3}CO_2Me + \cdot CH_2CH_2CO_2Me$$

$$Me\cdot + \cdot CH_2CH_2CO_2Me \rightarrow MeCH_2CH_2CO_2Me$$

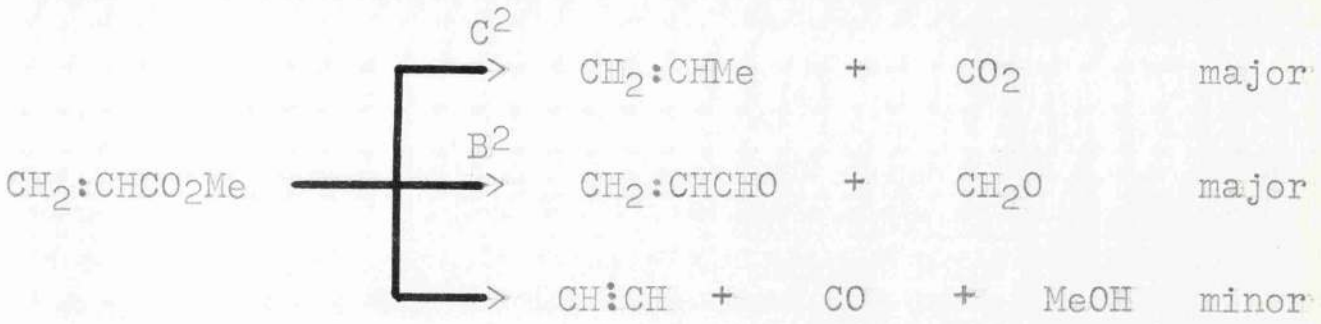
This tentative proposal has the advantage of accounting for the butyrate without any associated products, in accordance with the analytical results.

2.4.7. Trace Products.

Analysis of the constituents of pyrolysates was complete to greater than 98 % in all instances, but the adipate and sebacate each gave three trace components which could not be identified by gas/liquid chromatography. Data are given in table 7, Section 3.3.

2.4.8. Secondary Decomposition.

B^2 scission of the simple esters has already been considered. A three-route breakdown has been established for methyl acrylate(55)



A minor decomposition of the acrylate was established by identification of the above products. In general secondary breakdown was not extensive.

2.5. Pyrolysis of Methyl Esters of Monobasic Acids.

It was necessary for the elucidation of the thermal breakdown of methyl esters of dibasic acids to have information on the behaviour of simple esters under pyrolysis conditions. The compound were chosen to provide solutions to particular problems and for this reason, the results are not, in all cases, complete representations of the decompositions.

2.5.1. Pyrolysis of Methyl Propionate.

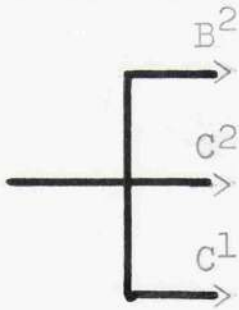
Methyl propionate was a major component of the methyl succinate and adipate pyrolysates, both of which contained compounds which can be attributed to secondary breakdown of the propionate from the present examination.

A single pyrolysis at 500° gave 17 % decomposition and a gas containing 6.1 % carbon dioxide, 8.4 % ethylene, 50 % carbon monoxide, 21.3 % saturated gases, methane and ethane, and 14.2 % hydrogen. The liquid pyrolysate contained methyl

formate and acetate, methanol and propionaldehyde, while formaldehyde was condensed in the cold trap at - 80°. Traces of methyl n-butyrate and propionic acid were also found.

B^2 scission is confirmed by formation of propionaldehyde and formaldehyde but the latter was, surprisingly, in excess in spite of its known, ready decomposition to hydrogen and carbon monoxide(85). Hydrogen and part of the carbon monoxide were attributed to this source, and decarbonylation of propionaldehyde gave ethane.

A clue to the source of the additional formaldehyde is found in the presence of methyl formate, which is known to be relatively unstable at 500°, one route giving two moles of formaldehyde(55).



	B^2 →	$2CH_2O$		minor
HCO_2Me	C^2 →	CH_4 +	CO_2	trace
	C^1 →	CO +	MeOH	major

Methanol may also arise from this reaction but the formation of methyl formate must be considered. Direct elimination is most probable, being supported by the presence of ethylene.

$$EtCO_2Me \rightarrow CH_2{:}CH_2 + HCO_2Me$$

An analogy is found in the intra-acyl scission of phenyl acrylate(61).

$$CH_2{:}CHCO_2Ph \rightarrow CH{:}CH + HCO_2Ph$$

The scission of the saturated ester is of relatively less importance. A similar elimination has been established for methyl succinate and methylsuccinate.

Peytral(25) detected acetic acid in the breakdown products of methyl acetate. Propionic acid from methyl propionate should arise from this A^O scission, thus;

$$EtCO_2Me \rightarrow EtCO_2H + \tfrac{1}{2}CH_2{:}CH_2 \quad \ldots A^O$$

It is a minor route, contributing only a small part of the total ethylene.

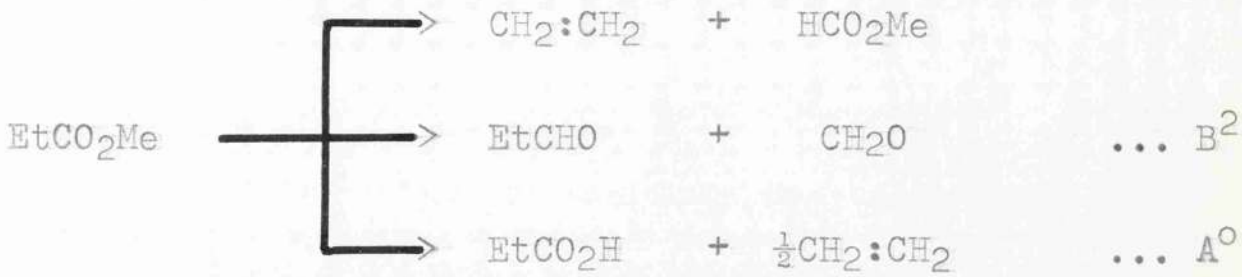
Two most surprising products were methyl acetate and n-butyrate. The former was present in significant quantity and the postulated mechanism for its formation from the methyl esters of dibasic acids is considered to be the most reasonable explanation. Existence of $\cdot CO_2Me$ and $Me\cdot$ radicals is assumed from the identification of methyl formate, condensation of these giving the acetate, thus;

$$Me\cdot + \cdot CO_2Me \rightarrow MeCO_2Me$$

No similar mechanism will yield methyl n-butyrate and the evidence is insufficient to justify a more complicated interpretation; the question is therefore left open.

The following scheme gives the confirmed breakbown

routes.



Secondary decomposition of methyl formate and formaldehyde is great, accounting for methanol and other gaseous products.

2.5.2. Pyrolysis of Methyl Vinylacetate and Allylacetate.

From the previous discussion(Section 2.4.2), these compounds were possible but unobserved products from the pyrolysis of methyl glutarate and adipate. Points of interest are the relative thermal stability and whether methyl acrylate could be formed from either.

Pyrolysis at 500° showed less than 50 % decomposition in each case and the gas analyses were;

	CO_2	C_2H_2	Olefin	CO	Sat.H/C.	H_2
Methyl vinylacetate	4.5	t	8.1	77.6	0.8	10
Methyl allylacetate	2.7	1.3	3.6	81.8	1.2	9.4

The olefin was ethylene and the saturated gases mainly methane. Small amounts of methyl formate, methanol and an acid were detected but methyl acrylate was absent. The Davidson and Newman test(88) gave a positive reaction indicating a trace of anhydride.

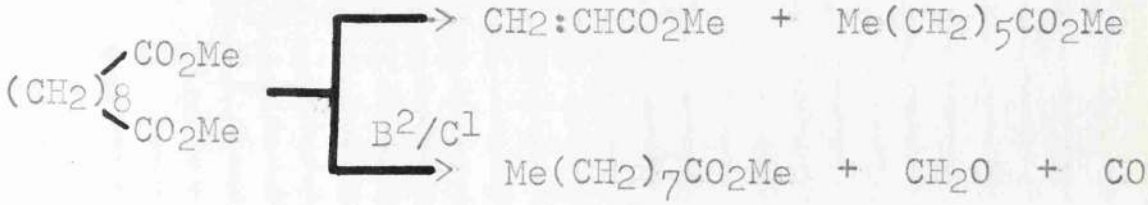
It may be concluded that failure to detect methyl vinylacetate and allylacetate in the pyrolysates from methyl glutarate and adipate cannot be a result of total decomposition, nor is methyl acrylate formed by them. No further information pertaining to the present work would be obtained so the investigation was not continued.

2.5.3. Pyrolysis of Methyl n-Nonoate and n-Heptoate.

Phenyl esters of lauric, palmitic and stearic acids undergo thermal scission at the β:γ-carbon bond(96) to give phenyl acrylate and a paraffin.

$$RCH_2CH_2CO_2Ph \rightarrow RH + CH_2{:}CHCO_2Ph$$

Chain length should not be of any significance, with the proviso that it exceeded four; thus methyl n-nonoate and n-heptoate were considered suitable to test the occurrence of this reaction in methyl esters. They would also yield information directly applicable to the breakdown of methyl sebacate as both are possible products from this compound, thus;



Gas/liquid chromatography did not separate these esters from methyl sebacate but their presence was strongly indicated.

a) Methyl n-nonoate.

A relatively short residence time, 4.9 seconds, caused 47 % breakdown at 500° while a feature of the gas analysis, (6.4 % carbon dioxide, 22.2 % monoxide, 38.3 % olefin, 26 % saturated hydrocarbons and 7.1 % hydrogen) was the major component, an olefin, whereas pyrolysis of other methyl esters gave carbon monoxide as the principal gaseous product. The olefin and saturated gases were not identified owing to the unavailability of the infrared spectrometer.

The liquid pyrolysate was separated into two rough fractions; i) 62 - 72° and ii) 160 - 195°. The decomposition was undoubtedly complex as the first fraction contained no less than ten constituents. Methyl acrylate and a minor quantity of n-hexane confirmed β:γ-bond rupture.

$$Me(CH_2)_7CO_2Me \longrightarrow Me(CH_2)_4Me + CH_2{:}CHCO_2Me$$

The paraffin is stable at 518° at atmospheric pressure(99), so secondary decomposition does not account for the shortage. Carbon-chain rupture is not confined to the β:γ-position, as shown by the formation of methyl n-heptoate, thus methyl acrylate may not come entirely from the n-nonoate, rather arising in a complex reaction which yields only minor amounts of n-hexane. Logically ethylene would be the olefin associated with methyl n-heptoate, formed thus;

$$Me(CH_2)_7CO_2Me \rightarrow Me(CH_2)_5CO_2Me + CH_2{:}CH_2$$

15 -20 % of the total decomposition was estimated to occur by this route, explaining the high olefin yield.

The presence of methyl formate requires no comment as its formation has been discussed for other esters. It was accompanied by methanol, formaldehyde and probably methane as expected(55,94). Acrolein would come via B^2 scission of methyl acrylate.

Acyl-oxygen scission of methyl pelargonate(n-nonoate) would give pelargonaldehyde. Although this was not identified, n-octane and formaldehyde confirmed the route.

$$Me(CH_2)_7CO_2Me \rightarrow Me(CH_2)_7CHO + CH_2O$$

$$Me(CH_2)_7CHO \xrightarrow{Cl} Me(CH_2)_6Me$$

Formaldehyde decomposes to hydrogen and carbon monoxide.

The radical mechanism proposed for the formation of methyl acetate is applicable from the presence of methyl formate. It is consistent with the complexity of the total breakdown.

Of six substances detected in the higher boiling fraction, n-octane, n-heptaldehyde, methyl n-heptoate and unchanged methyl n-nonoate were definitely identified. Elimination of formaldehyde from the n-heptoate yields the corresponding

aldehyde.

From the results it appears that the work required for a complete analysis and interpretation of the findings would be totally disproportionate to the relevant information provided. For this reason the investigation was abandoned at this stage; however, complete chromatographic data are included in Table 7, Section 3.3.

b) Methyl n-heptoate.

Methyl n-heptoate is slightly more stable than the n-nonoate, 58 % surviving pyrolysis at 500° and residence time of 5.1 seconds. An olefin was again the largest component of the gases, analysis showing 6.6 % carbon dioxide, 34 % olefin, 22.8 % saturated hydrocarbons, 22.8 % carbon monoxide and 9.0 % hydrogen. The liquid separated into two rough fractions i) 58 - 76° and ii) 158 - 170°.

Six compounds, in identifiable quantity, and three uncertain traces were found in fraction i). Methyl acrylate was the principal product but the presence of n-butane could not be proved without the aid of infrared spectroscopy.

$$Me(CH_2)_5CO_2Me \rightarrow CH_2{:}CHCO_2Me + Me(CH_2)_2Me$$

An equivalent amount of n-butane would only be formed by a simple scission. This does not seem probable from the behaviour of methyl n-nonoate.

Elimination of methyl formate from an ester is

postulated, but the particular source is not specified as more than one exists. Secondary decomposition of the formate was also confirmed. These observations admit the application of the radical mechanism to the formation of methyl acetate

The importance of B^2 scission is evidenced by the quantity of formaldehyde and n-heptaldehyde, formed thus;

$$Me(CH_2)_5CO_2Me \rightarrow Me(CH_2)_5CHO + CH_2O$$

This accounted for 10 - 15 % of the breakdown.

A more detailed scheme was not looked for as the pertinent questions have been answered.

The most important point reported here is the new reaction of the methyl esters of long, straight-chain, monobasic acids which yields methyl acrylate. Surprisingly, these esters have a more complex pyrolysis than the corresponding esters of dibasic acids, carbon-chain rupture occurring at more than one site.

2.6. Comparison of Thermal Stability of Esters.

An indication of the relative stability of compounds may be obtained by measurement of the percentage decomposition, in the flow pyrolysis apparatus, at identical residence times. Exact control of the feed flow-rate, and therefore of the residence time, is difficult and tedious, while quantitative analysis is not sufficiently accurate for differentiation of compounds of similar stability.

"Onset" Temperatures of Esters of Straight Chain Saturated Dibasic Acids.

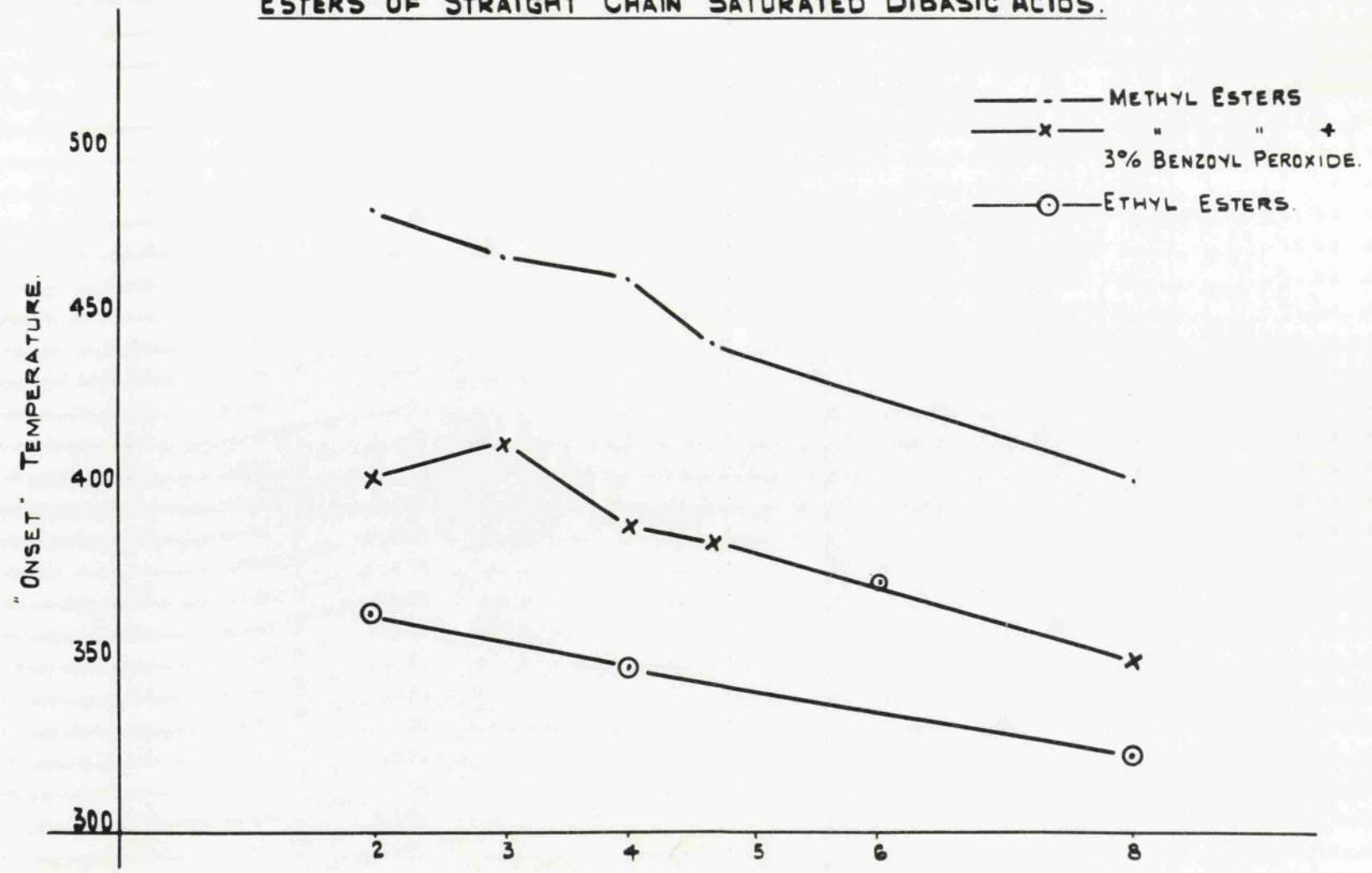


Fig. IV

The apparatus devised by Mackinnon and Ritchie(100) for the measurement of 'threshold' temperatures has been modified(Section 3.1.4.) and applied to the present work. Basically it is a static reactor through which a stream of nitrogen is passed while the temperature is gradually raised. Volatile products are carried to a detection cell and the temperature of first evolution recorded.

Comparison of stabilities is made by determination of the 'onset' temperature, defined for the present purpose as the lowest temperature at which detectable decomposition occurs under standard conditions. This is preferred to 'threshold' temperature, regarded as the temperature at which a particular product was evolved, because it allows comparison of esters both with and without β-hydrogen.

The absolute significance which may be placed on 'onset' temperatures is uncertain. Work by Boyd(101), using the modified apparatus, showed the values to be reproducible under varying gas flow and heating rates and with reactors of different sizes. By following the pressure-temperature CHANGES, Norris(102) concluded that there was a definite temperature at which decomposition occured and in complex breakdown each route appeared at a fixed temperature. External conditions do have an effect as shown by the behavior of n-hexane, stable at 500° under atmospheric pressure(98) but decomposing explosively at high pressure(104).

In the present discussion only the relative values are

considered; thus, irrespective of the true meaning of the temperatures, an accurate comparison is obtained. The 'onset' temperatures for the ethyl and methyl esters of saturated dibasic acids are plotted against methylene groups, Fig. IV, the third curve being for methyl esters containing 3 % benzoyl peroxide. A similar graph could be constructed using the molecular weight as the abscissa.

Stabilities appear to decrease approximately linearly with increasing molecular weight. Flow pyrolysis measurements, for the ethyl esters, were in rough agreement, Table 3.

Table 3.

Pyrolysand	I	V	VIII	X	XI	XII	XIII
Mol. wt.	174	202	288	146	174	160	230
% Decomp.	92	96	98	23.5	24.7	24.9	26.0

It is seen that methyl esters give less concordant figures. Absence of β-hydrogen gives a marked increase in 'onset' temperature, as expected. Methyl methylsuccinate is more stable than isomeric methyl glutarate which suggests participation of hydrogen in the α-position, any effect of the methyl substituent on the methyl of the ester group being improbable.

A similar relationship between molecular weight and stability was found by Smith and Wetzel(103) who compared ethyl esters of a series of straight chain, monobasic acids by calculation of 'characteristic' temperature - temperature

at which a maximum is obtained on the plot of % yield/ pyrolysis temperature versus pyrolysis temperature. In effect it is the temperature at which most efficient pyrolysis takes place. Characteristic temperature increases inversely with molecular weight in a zig-zag manner, esters with an odd number of methylene groups having relatively higher values.

Direct evidence of radical initiation of thermal breakdown is found in the set of readings obtained for the methyl esters containing benzoyl peroxide, a known source of free radicals(106). These were 50 - 80° lower than for the pure esters indicating that presence of radicals facilitated decomposition. The presence of the initiator did not significantly effect the comparative values.

Ethyl suberate gave an anomolous 'onset' temperature which did not fit the general scheme. No explanation can be advanced as the decomposition has not been studied.

2.7. Reaction Mechanisms in the Pyrolysis of Esters.

The mechanisms of pyrolytic reactions been the subject of much research, but because of the complexity of the kinetics, remain controversial. The A^1 scission has been most widely studied and the cyclic transition state is generally accepted, the work of Barton, Head and Williams(34) on (-)-menthyl benzoate confirming first order kinetics and preference for cis-elimination. Most other decomposition

routes are competitive, not admitting simple measurement of reaction order. The B^2 scission would not be expected to differ in ethyl and methyl esters, thus only mechanisms for the breakdown of the latter are further considered.

The principal decomposition route of the methyl esters of saturated dibasic acids(hereinafter referred to as dimethyl esters) is that yielding methyl acrylate. A parallel has been drawn with the intra-acyl scission of phenyl acrylate(31) for which a radical mechanism was proposed.

Initiation:

$$CH_2{:}CHCO_2Ph \rightarrow CH_2{:}\dot{C}H + \cdot CO_2Ph$$

Propagation:

i $\quad CH_2{:}\dot{C}H + CH_2{:}CHCO_2Ph \rightarrow CH_2{:}CH_2 + \cdot CH{:}CHCO_2Ph$

ii $\quad \cdot CH{:}CHCO_2Ph \rightarrow CH{:}CH + \cdot CO_2Ph$

iii $\quad \cdot CO_2Ph + CH_2{:}CHCO_2Ph \rightarrow HCO_2Ph + \cdot CH{:}CHCO_2Ph$

The initiation step for dimethyl esters would be a simple scission giving two radicals but no highly favourable site exists. Hydrogen abstraction from an unchanged molecule can account for methyl acrylate, thus;

$$(CH_2)_n\begin{matrix}CO_2Me\\CO_2Me\end{matrix} + R\cdot \rightarrow (CH_2)_{n-1}\begin{matrix}CO_2Me\\ \cdot CHCO_2Me\end{matrix} + RH$$

$$\downarrow$$

$$CH_2{:}CHCO_2Me + \cdot CH_2(CH_2)_{n-3}CO_2Me$$

The final radical produced would replace R· in propagating the reaction, the saturated ester $Me(CH_2)_{n-3}CO_2Me$ being formed.

One initiating scission which would account for methyl formate may be considered.

$$RCH_2CO_2Me \rightarrow \dot{R}CH_2 + \cdot CO_2Me$$

The $\cdot CO_2Me$ or the methyl radical from its decomposition, could abstract hydrogen, thus;

$$RCH_2CO_2Me + \cdot CO_2Me \rightarrow \dot{R}CHCO_2Me + HCO_2Me$$

$$\cdot CO_2Me \rightarrow Me\cdot + CO_2$$

$$RCH_2CO_2Me + Me\cdot \rightarrow \dot{R}CHCO_2Me + MeH$$

The new radical is identical with that formed in the proposed propagation and will decompose to methyl acrylate, as shown. Detection of methane and carbon dioxide supports this interpretation and methyl acetate, another common product, can arise <u>via</u> a termination reaction, thus;

$$Me\cdot + \cdot CO_2Me \rightarrow MeCO_2Me$$

The quantities of acetate found indicate that the number of hydrogen transfers in a given chain reaction will be small.

Methyl <u>n</u>-butyrate could arise from more than one scission of the adipate and sebacate but rupture of a

β:γ bond is consistent with the saturated ester products and the availability of methyl radicals.

$$CH_2CH_2CO_2Me \backslash (CH_2)_{n-2}CO_2Me \rightarrow \cdot CH_2CH_2CO_2Me + \cdot CH_2(CH_2)_{n-3}CO_2Me$$

$$Me\cdot + \cdot CH_2CH_2CO_2Me \rightarrow MeCH_2CH_2CO_2Me$$

Although the quantity was again large to arise from a termination no transfer reaction nor other primary scission would fit the experimental findings.

Care must be exercised in interpretating the effect of benzoyl peroxide on the 'onset' temperatures as it lowered the temperature at which formaldehyde was evolved. B^2 scission and methyl formate would both give this product. The actual reaction which is initiated cannot be ascertained but there can be no doubt that free radicals participate in the breakdown, giving a basis for the above proposed mechanism. The peroxide decomposes in the region of 100°(106) to benzoyl and phenyl radicals and hydrogen abstraction does not require more vigorous conditions(105). The following scheme is proposed to represent the formation of methyl acrylate.

i $RCH_2CH_2CO_2Me + Ph\cdot \rightarrow RCH_2\dot{C}HCO_2Me + PhH$

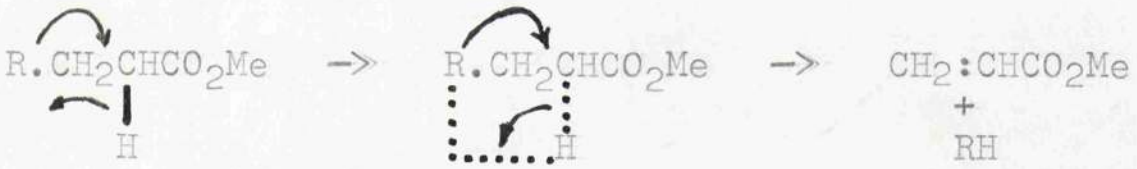
ii $RCH_2\dot{C}HCO_2Me + RCH_2CH_2CO_2Me \rightleftharpoons RCH_2CH_2CO_2Me + RCH_2\dot{C}HCO_2Me$

iii $RCH_2\dot{C}HCO_2Me \rightarrow CH_2{:}CHCO_2Me + R\cdot$

Initial hydrogen abstraction is represented by i, while a dynamic equilibrium, ii, is set up until the 'onset' temperature is reached when decomposition, iii, occurs. Agreement with the known chain transfer reactions(105,106) may thus be achieved. Radical formation from benzyl esters of acetic and formic acids, which lack β-hydrogen, was illustrated by Szwarc and Watson(107), who found bond dissociation energies corresponding to the scission;

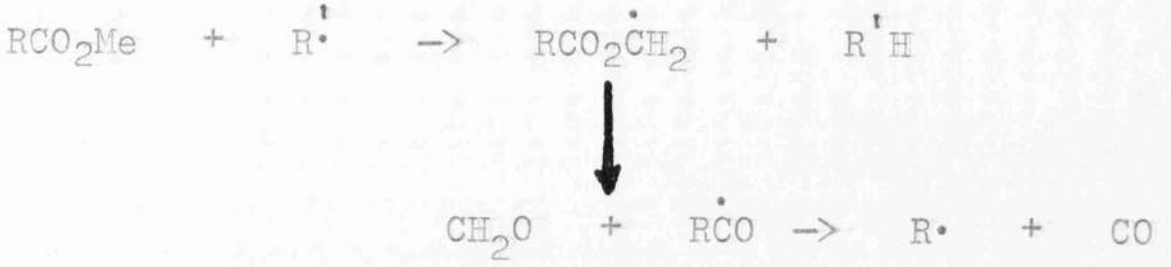
$$AcOCH_2Ph \rightarrow AcO\cdot + \cdot CH_2Ph$$

A molecular mechanism can be advanced for the formation of α:β-unsaturated esters, thus;

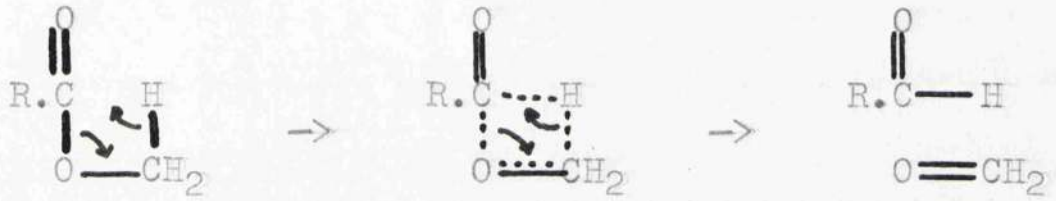


Unsaturated triad systems exhibit this type of hydrogen migration(124) and the high energy available at 500° could facilitate it in a saturated molecule. However a strong objection is the absence of side reactions which are necessary to account for the variety of products.

Hurd and Blunck(28) have suggested that B^2 scission is a chain reaction, primary hydrogen abstraction being followed by decomposition of the resulting radical.



Decarbonylation of $R\dot{C}O$ accounts for the deficiency of the corresponding aldehyde. A four-membered cyclic transition state may be deduced but strong electromeric withdrawal would considerably weaken it.



This is not acceptable on the grounds of the unfavourable structure and the comparatively low yield of the higher molecular weight aldehyde.

Two facts favour a radical mechanism over a molecular interpretation. The complex pyrolysates are more easily explained by the former and the effect of benzoyl peroxide on the 'onset' temperature indicates radical initiation. Further evidence for occurrence comes from the work of Swarski and Burton(43) and Niclause(46), showing decarbonylation of aldehydes, a known secondary reaction in the breakdown of methyl esters, to be a chain reaction. The high stability of methyl esters is consistent with the initiation energy required for primary scission to two radicals.

2.8. Pyrolysis of Anhydrides.

Monobasic acids have been found to be thermally stable and only acetic acid was known to dehydrate thermally(15). Recent work by Davidson and Newman(88) has shown the earlier observations to be in error, most monobasic acids giving small quantities of anhydride at 200 - 250°. Partial dehydration of acids must therefore be expected in pyrolyses at 500° and knowledge of the behavior of anhydrides is essential.

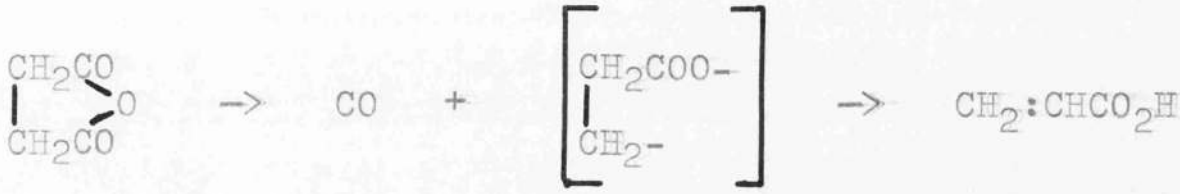
2.8.1. Pyrolysis of Succinic Anhydride.

This five-membered cyclic anhydride was not particularly stable at 500°, 50 - 55 % decomposing, while at 585° only 20 - 25 % survived. A typical gaseous pyrolysate contained 29.2 % carbon dioxide, 10.65 % ethylene, 60.2 % carbon monoxide and a trace of acetylene. The liquid product was acrylic acid containing a trace of acrolein while the solid was entirely unchanged anhydride.

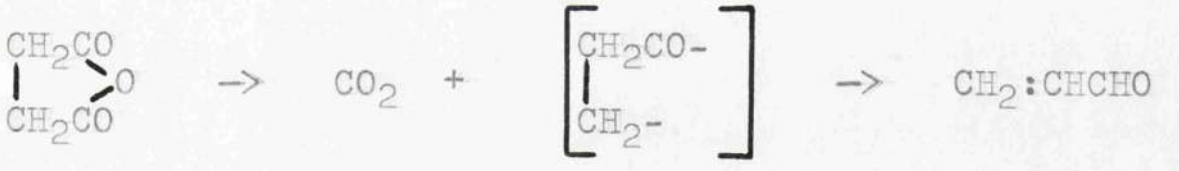
Breakdown of succinic anhydride has been examined at temperatures of 800 - 900°(73), equimolar quantities of carbon monoxide, dioxide and ethylene being the only recorded products. At 250 - 280° a condensation, with elimination of carbon dioxide, occurs giving the spiro-dilactone of acetonediacetic acid(71). Attempts to isolate the dilactone were conclusively negative; thus, if formed, it must be completely decomposed at the ambient temperature in the

reactor.

Loss of a mole of carbon monoxide from an anhydride molecule gives a fragment which could rearrange to acrylic acid, the major product.

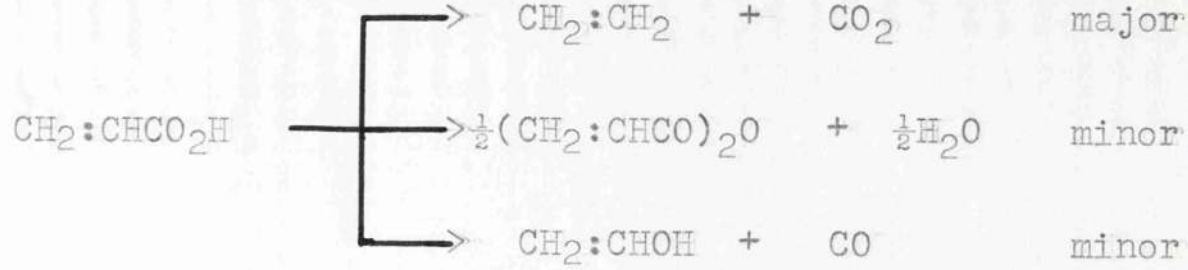


Decarbonylation was the primary step suggested for the formation of the dilactone, the fragment adding to an unchanged anhydride molecule(71). Internal rearrangement is probably favoured by the higher temperature. Similarly, acrolein is accounted for by loss of a mole of carbon dioxide followed by hydrogen migration, thus;



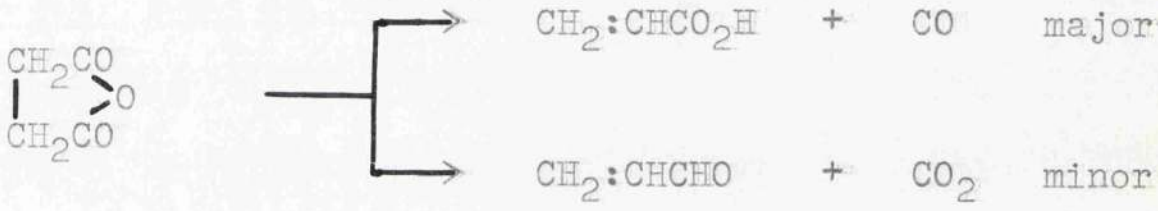
Both routes require rupture of a -CO-O- bond but subsequent elimination of carbon monoxide is strongly preferred.

Exclusive decarbonylation of acrolein(48) and the three-route breakdown of acrylic acid(48) are probable secondary reactions.



Neither acetaldehyde, via rearrangement of vinyl alcohol, nor acrylic anhydride were detected but decomposition of the latter(Section 2.8.6) would account for the trace of acetylene.

A two-route breakdown of succinic anhydride occurs at 500°.



The less stable acrolein is regarded as the main source of ethylene, acrylic acid undergoing only minor secondary decomposition.

2.8.2. Pyrolysis of Methylsuccinic Anhydride.

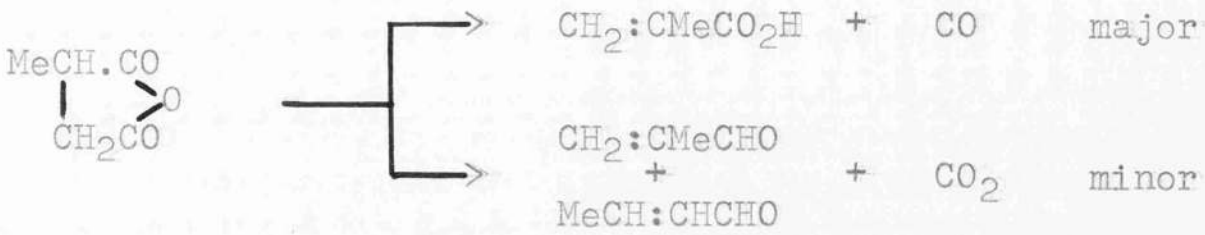
The most obvious effect of the methyl substituent is an increase in thermal stability. Decomposition was negligible at 500°, while at 550° and 600°, 50 % and 10 % survived respectively. Gas analysis gave the following;

	CO_2	CH:CMe	Olefin	CO	
Pyrolysis at 550°	18.7	-	18.4	62.9	%
" " 600°	30.8	0.8	51	17.4	%

The olefin was mainly propene. The solid product was unchanged pyrolysand and the liquid contained a major quantity of α-methylacrylic acid and smaller amounts of α-methylacrolein and crotonaldehyde.

By analogy with succinic anhydride a major decarbonylation

and a minor decarboxylation are proposed.



Absence of α-crotonic acid is surprising since both aldehydes were identified. A blocking effect of the methyl group should act equally in both routes unless the mechanisms differ. This point is discussed in Section 2.8.7.

The improvement of stability by replacement of one α-hydrogen is interesting. It is comparable with the high stability of α:α'-tetramethyladipic anhydride whereas the unsubstituted adipic anhydride decomposes at its boiling point(70) It is concluded that α-hydrogen has an important role in decomposition of anhydrides.

2.8.3. Pyrolysis of Maleic Anhydride.

Rice and Murphy(73) obtained an equimolar mixture of carbon dioxide, monoxide and acetylene from pyrolysis of maleic anhydride at 800 - 900°. It was of interest to determine whether acidic and aldehydic intermediates could be isolated at lower temperatures.

Pyrolyses at 430° and 500° gave only gaseous products, the extent of decomposition being 9 % and 50 % respectively. The gas formed at 500° consisted of approximately equal quantities of carbon dioxide, monoxide and acetylene but that

from obtained at the lower temperature showed a deficiency of monoxide and acetylene. Negligible breakdown was observed at 350°.

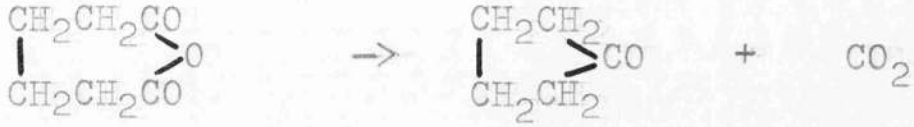
Propiolic acid and propiolaldehyde are the possible intermediates. The acid is known to readily decarboxylate at its boiling point(108) which accounts for its non-detection. 50 % propiolaldehyde survived pyrolysis at 500°. The reaction was not simple, 30 % of the pyrolysate being a carbonaceous deposit on the reactor. Decarbonylation was a minor route, as shown by the gas analysis, 4.2 % carbon dioxide, 7.8 % acetylene, 4.0 % ethylene and 83.9 % carbon monoxide. Addition of each drop of pyrolysand was accompanied by a flash suggesting a highly exothermic reaction. A similar occurrence was reported in the pyrolysis of acetylene(109) and attributed to polymerisation,which could apply here, the polymeric aldehyde losing carbon monoxide which would account for the excess of this gas. The liquid pyrolysate was pure propiolaldehyde.

The possibility of unstable intermediates is unconfirmed while the moderate carbonisation is inconsistent with other than very minor quantities of the aldehyde. No liquid triple-bond compounds were detected.

2.8.4. Pyrolysis of Monomeric Adipic Anhydride.

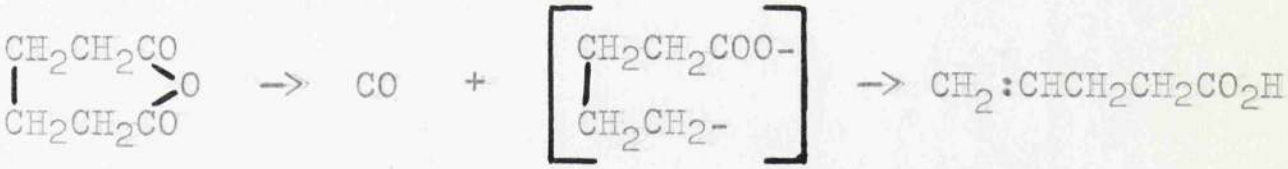
Monomeric adipic anhydride obeys the Blanc Rule(68) for the formation of cyclic ketones under relatively mild

conditions.



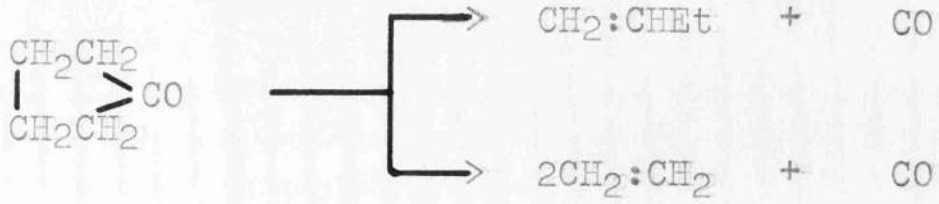
At 500° decomposition was effectively 100 % and the above reaction was confirmed as the major route. A gas, 83.2 % carbon dioxide, 10.4 % monoxide, 6.75 % ethylene and a trace of but-1-ene, was obtained and a little allylacetic acid was also identified.

The unsaturated acid is the most interesting product. A new breakdown route can be postulated, namely elimination of carbon monoxide with rearrangement of the residual fragment.



No previous record exist. At lower temperatures cyclopentanone is the exclusive product.

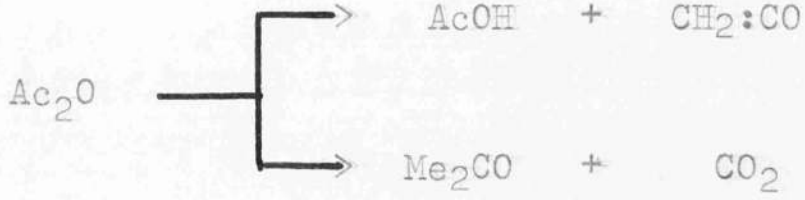
The gaseous olefins can both arise from cyclopentanone(90)



A second possible source of n-but-1-ene is decarboxylation of allylacetic acid. Some contribution is probably made by each route.

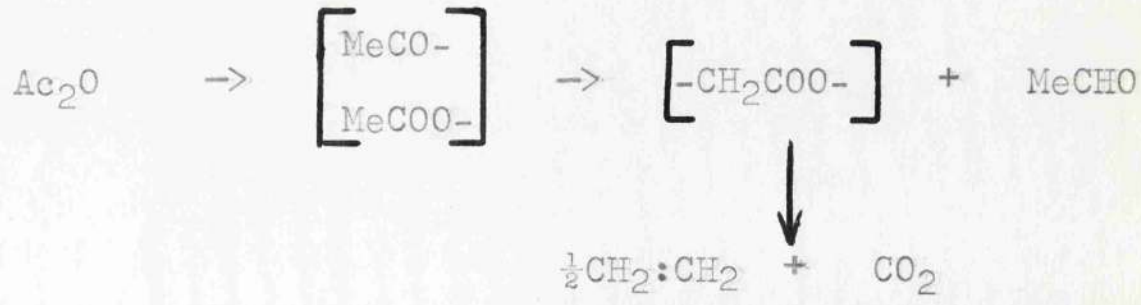
2.8.5. Pyrolysis of Acetic Anhydride.

Thermal breakdown of acetic acid is well established, by Szwarc and Murawski(65) and Davidson and Newman(67), to occur by two routes.



Both were confirmed at 500° in a 70 - 75 % decomposition, which also gave 36.9 % carbon dioxide, 42 % monoxide, 13.2 % ethylene, 7.9 % methane and a trace of acetylene in the gas and a significant quantity of acetaldehyde.

Acetaldehyde deserves comment. It is not known to arise from any of the primary products. A mechanism based on rupture of a -CO-O- bond, which is necessary for the formation of acetic acid and keten, would be the most acceptable, hydrogen transfer between the fragments giving the aldehyde.



The gases are not confirmatory as carbon dioxide is a co-product with acetone, and keten yields principally ethylene(64) on decomposition.

2.8.6. Pyrolysis of Acrylic and α-Methylacrylic Anhydrides.

These unsaturated anhydrides are not of direct interest in the present work but provide information relevent to the study of the pyrolysis of acrylates(55) and α-methyl-acrylates(48).

a) Acrylic Anhydride.

In two pyrolyses at 500°, 12 % and 17 % acrylic anhydride remained undecomposed while the gases had similar composition, analysis of the first being 15.4 % carbon dioxide, 18.1 % acetylene, 8.38 % ethylene and 58.2 % carbon monoxide. A trace of acrolein was identified with the main product, acrylic acid.

An acidic product from an anhydride is normally associated with keten formation. In this case the latter, methylene keten, would be extremely unstable and is the probable precursor of acetylene and carbon monoxide.

$$(CH_2{:}CHCO)_2O \rightarrow [CH_2{:}C{:}CO] + CH_2{:}CHCO_2H$$

$$\downarrow$$

$$CH{:}CH + CO$$

It is possible that the keten has no real existence, acetylene and carbon monoxide being produced directly.

Acrolein is less easily explained. Carbon dioxide loss from the anhydride would give divinyl ketone which, although not found, could decompose completely to acrolein by the

general reaction for ketones(15), thus;

$$(CH_2{:}CHCO)_2O \rightarrow \left[(CH_2{:}CH)_2CO\right] + CO_2$$

$$\downarrow$$

$$CH{:}CH + CH_2{:}CHCHO$$

Alternatively, if no ketone is formed, the reaction will be equivalent to that of acetic anhydride.

$$(CH_2{:}CHCO)_2O \rightarrow \left[-CH{:}CHCOO-\right] + CH_2{:}CHCHO$$

$$\downarrow$$

$$CH{:}CH + CO_2$$

The end-products are identical, preventing differentiation of the routes. However, the major decomposition to the acid, acetylene and carbon monoxide is established.

b) <u>α-Methylacrylic Anhydride</u>.

α-Methylacrylic acid, in quantity, and a trace of α-methylacrolein indicated that breakdown was similar to acrylic anhydride, but a superior stability was imparted by the methyl group. Carbon dioxide 26.5 %, methylacetylene 0.9 %, propene 11.1 % and carbon monoxide 56.2 % comprised the gaseous pyrolysate. The -80° trap also contained methylacetylene.

The α-methyl group obstructs formation of a keten so methylacetylene and carbon monoxide will be primary products with the acid, thus;

$$(CH_2{:}CMeCO)_2O \rightarrow CH_2{:}CMeCO_2H + CH{:}CMe + CO$$

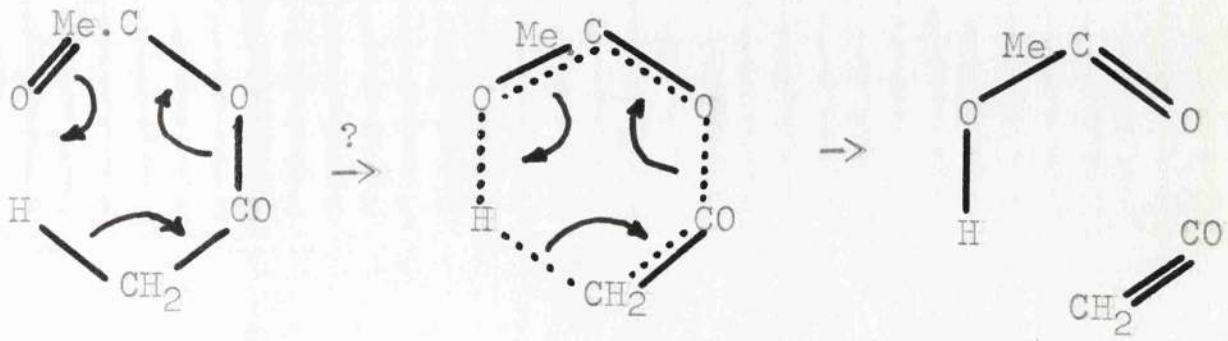
The arguments applied to the pyrolysis of acrylic anhydride to acrolein are revelent to the formation of α-methylacrolein. It can come directly from the pyrolysand or via the unstable intermediate, isopropenyl ketone.

$$(CH_2{:}CMeCO)_2O \xrightarrow{-CO_2} \left[(CH_2{:}CMe)_2CO\right] \rightarrow CH{:}CMe + CH_2{:}CMeCHO$$

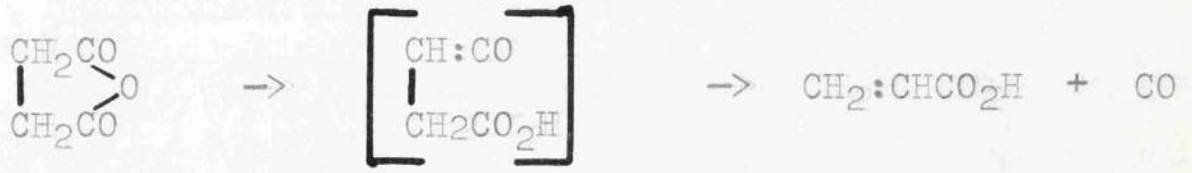
Although these routes cannot be distinguished, the end-products and also the major breakdown of α-methylacrylic anhydride to the acid are confirmed.

2.8.7. Reaction Mechanisms in the Pyrolysis of Anhydrides.

The breakdown of acetic anhydride to acetic acid and keten is unimolecular, Szwarc and Murawski(65), requiring an intramolecular mechanism. A cyclic transition state, similar to that for A^1 scission of esters(12,34), is proposed.



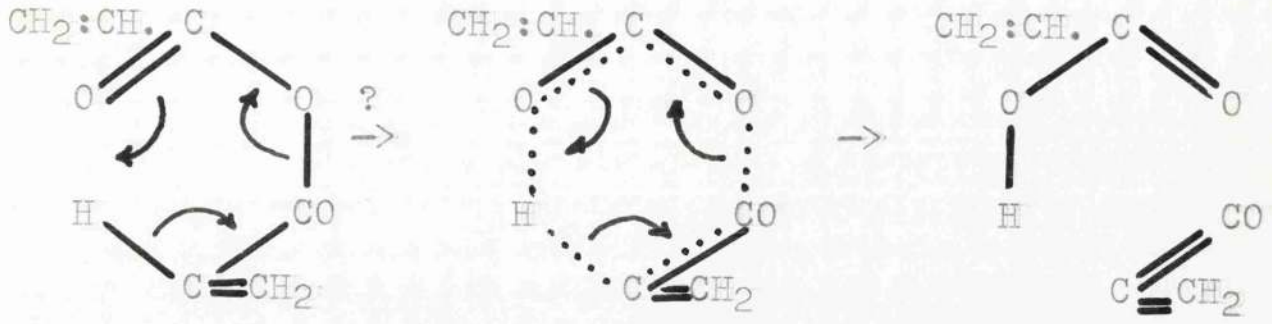
Application to any anhydride having α-hydrogen is possible, but where β-hydrogen is available the keten is unstable(66). Cyclic anhydrides of dibasic acids would form strained, bicyclic transition compounds, the resulting keten and acidic functional groups being in a single molecule.



The methyl substituent of methylsuccinic anhydride will interfere in the transition state, thus hydrogen transfer from the unsubstituted carbon would be favoured;

This explains the exclusive formation of α-methylacrylic acid and absence of α-crotonic acid.

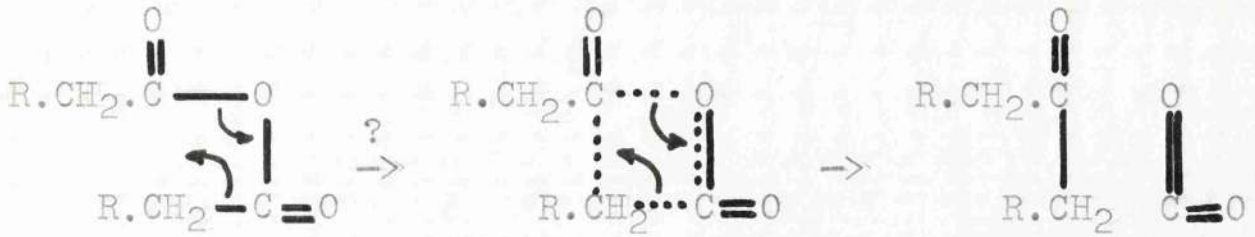
α:β-unsaturation increases the resonance energy of the transition state as one double bond would be in conjugation with the partial double bonds. The highly strained structure of the keten will render it very unstable and none has ever been isolated, although expected products(64) from secondary breakdown have been confirmed.



When the α-hydrogen is replaced by a methyl group thermal stability is considerably greater but, surprisingly, the formation of acid is not prevented, which suggests a second mechanism is possible. This latter is obscure.

The cyclic transition state fulfils the conditions, of the Principle of Least Motion(24), of minimum electronic displacement and maximum resonance; also, the importance of α-hydrogen has been illustrated by the increased stability when wholly or partly replaced by a substituent. The main negative indication is the formation of α-methylacrylic acid from the anhydride which has no α-hydrogen.

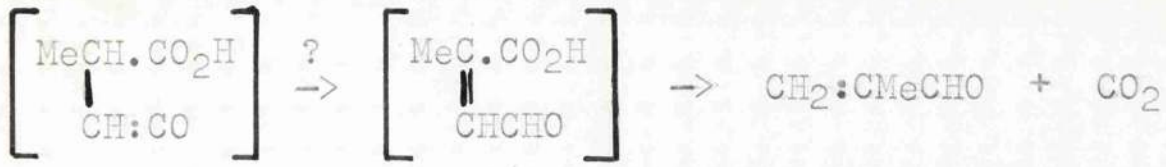
Ketone formation is general in the competitive breakdown of the anhydrides of monobasic acids(67), and for seven and eight-membered cyclic compounds it is an exclusive reaction in the range 200 - 300°. Participation of the α-hydrogen was confirmed by the non-formation of a cyclic ketone from α:α'-tetramethyladipic anhydride. Kinetic evidence is not available but a molecular mechanism is postulated on the basis of the relatively mild conditions for decomposition of the cyclic anhydrides.



R may be hydrogen or any alkyl group, while in the cyclic anhydrides both are replaced by a methylene chain. In the latter case the transition compound will consist of a four and a five or six-membered ring.

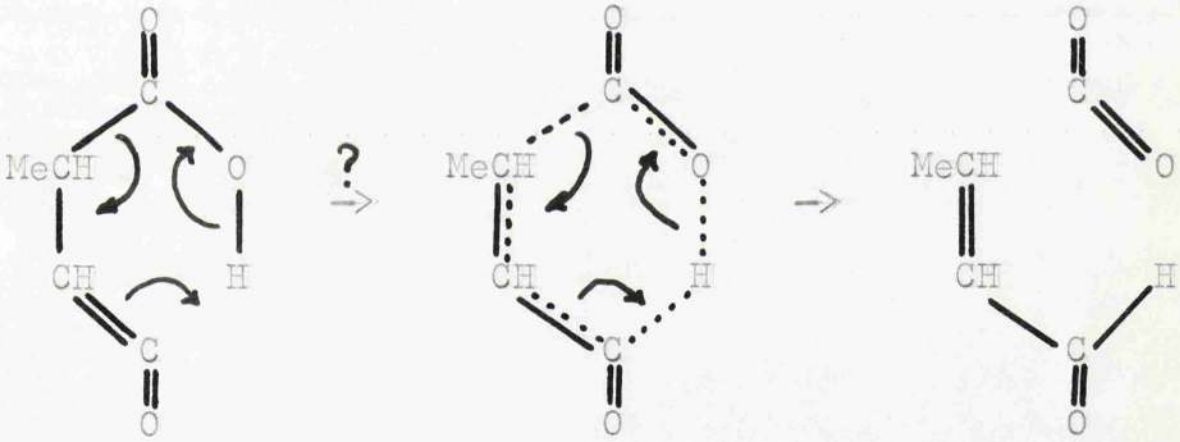
The requirements of the Principle of Least Motion are satisfied by the above. The difference in ease of reaction is explained by the preference, in the breakdown of open-chain anhydrides, for the six-membered transition state which yields an acid, whereas transformation from a strained to a strainless five or six-membered ring structure is favoured in the decomposition of the cyclic anhydrides.

Uncertainity of the route to aldehydes limits discussion of a mechanism. If they are formed <u>via</u> ketones it is difficult to foresee a simple, low energy molecular mechanism, while the evidence is not sufficient to allow formulation of a mechanism for a direct route. An exception is the breakdown of succinic and methylsuccinic anhydrides where the postulated primary product, a keten-acid, could rearrange and undergo partial decarboxylation, thus;



A similar shift of the double bond in decarboxylation of β:γ-unsaturated acids has been reported by Arnold, Smith and Dodson(110), thus;

A modified form of the proposed cyclic mechanism may be applied here.



In general the pyrolytic reactions of anhydrides are better fitted to a molecular interpretation. The Principle of Least Motion(24) is obeyed and the observed structural effects are in agreement.

2.8.8. Conclusions.

The pyrolyses of methyl and ethyl esters of saturated dibasic acids at 500° are widely different. The latter decompose extensively by known reactions, while the former are relatively stable and show several new types of scission. Application of the results to the decomposition of polyesters is necessarily tentative as the detailed breakdown of saturated polymers is not known.

As would be expected from the presence of β-hydrogen, A^1 scission predominates in the ethyl esters while a minor B^2 scission is also general. The evidence showed no interaction between ester groups in a single molecule.

Absence of β-hydrogen greatly increases thermal stability and also the complexity of breakdown. Several general pyrolytic reactions have been established for the methyl esters. The most important and previously unobserved are the principal route yielding α:β-unsaturated esters and the minor reaction forming methyl formate. Aldehydic compounds also arise via B^2 scission. Other products are not attributable to simple routes, being more easily explained by a complex decomposition.

The mechanism of decomposition of the methyl esters has been discussed and a free radical reaction could account for the findings. This is supported by the high energy required, the numerous products and the effect of a radical initiator on the 'onset' temperatures.

The behaviour of saturated fragments of a polyester may be prdicted from the above conclusions. Where β-hydrogen is available only A^1 and B^2 scissions should occur as primary reactions. In absence of β-hydrogen thermal stability should be greater and decomposition would be expected to involve the methylene chain of the acid as well as the ester groupings. The relatively higher stability of methyl methylsuccinate indicates that α-substitution of the acid would have a beneficial effect on the polyester.

Two new decomposition routes are reported for five-membered cyclic anhydrides, yielding an unsaturated acid and aldehyde respectively, while adipic anhydride is shown to give a minor quantity of unsaturated acid in addition to the expected cyclopentanone(68). The decomposition of α:β-unsaturated anhydrides is analogous to that known for saturated compounds(67). Molecular mechanisms are postulated on the basis of the confirmed importance of the α-hydrogen and the absence of side-reactions.

Anhydride decomposition has accounted for unexpected products in the pyrolyses of ethyl esters showing acid dehydration to occur at 500°. It has also been shown to be significant in the breakdown of maleates and α-methylacrylates, (55) and acrylates(48).

3. EXPERIMENTAL.

3.1. Apparatus.

3.1.1. Flow Pyrolysis Apparatus.

Pyrolyses were carried out in a flow system, Fig. VI, in an atmosphere of oxygen-free nitrogen. Pyrolysand was admitted at the top of a vertical reactor and the products separated into rough fractions, liquids and solids, low boiling liquids condensed at -80° and gases. The choice of reactor depended on the quantity of material and the temperature desired.

Dimensions of the three vertical pyrolysis tubes are given in Fig. VII. A and B, constructed of Pyrex glass, differed only in size, the former being used for 15 g. pyrolysand or more and the latter for quantities down to 4 g. The third vessel, a silica tube, allowed temperatures above 550°, taking 1 - 10 g. pyrolysand. The Pyrex reactors were packed with ½ inch lengths of 6 mm. diameter tubing, C being filled with silica chips of 4 - 8 mm. diameter. The following are the characteristics of the furnaces;

Furnace	Length	Bore	Winding Resistance
A	46.0 cm.	5.3 cm.	35 ohms
B	25.5 cm.	3.5 cm	70 ohms
C	13.5 cm.	2.5 cm.	80 ohms

A Sunvic energy controller regulated the heating.

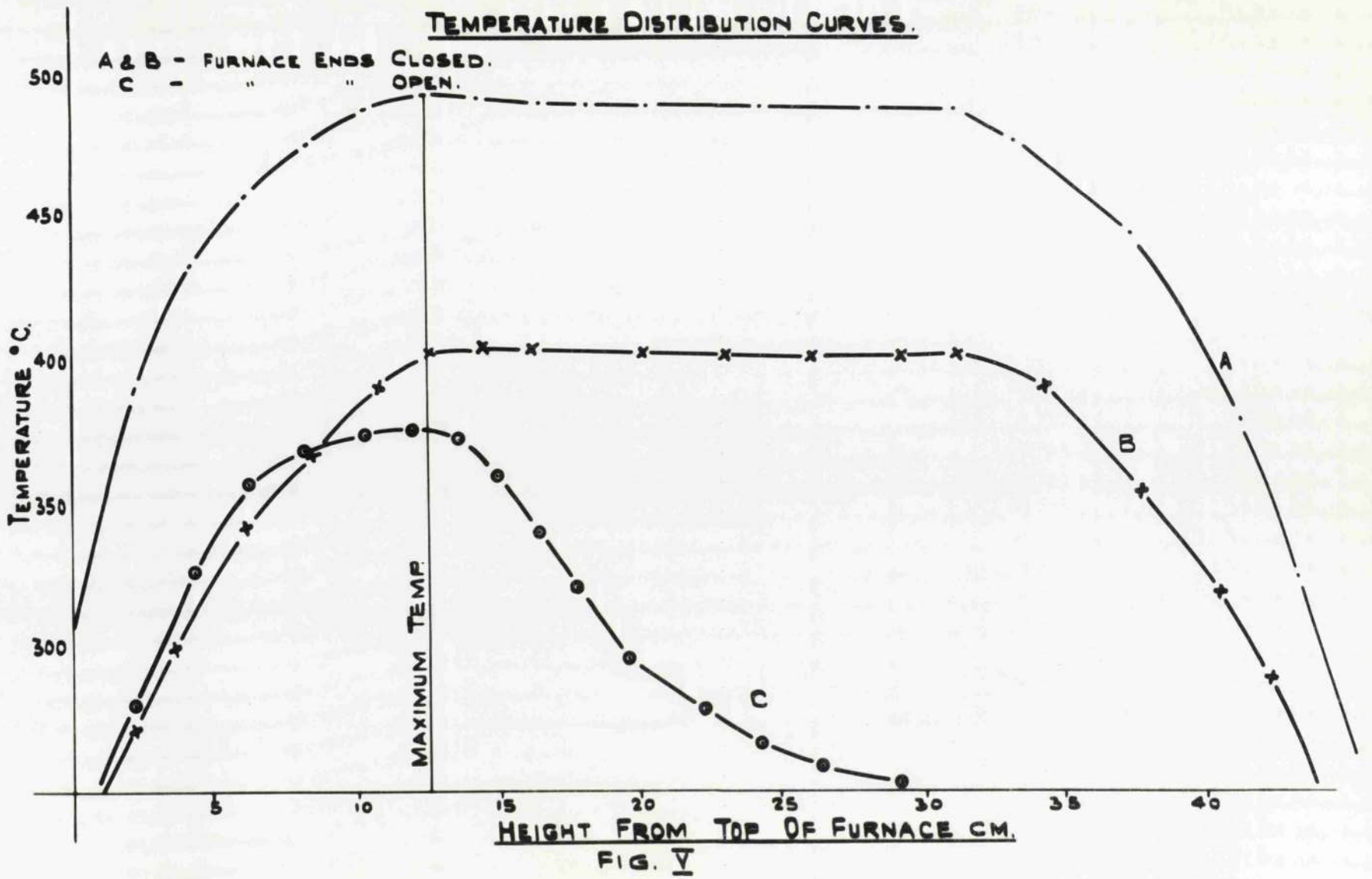

TEMPERATURE DISTRIBUTION CURVES.
A & B - FURNACE ENDS CLOSED.
C - " " OPEN.
500
450
400
350
300
TEMPERATURE °C.
MAXIMUM TEMP.
A
B
C
5
10
15
20
25
30
35
40
HEIGHT FROM TOP OF FURNACE CM.

FIG. V

Temperature of pyrolysis is regarded as the maximum in the reactor while the reaction volume, the packed section, is maintained within $\mp 5^{\circ}$ of this value. The temperature distribution curve, Fig. V, shows the range of temperatures in the reactor when both ends of the furnace were open and when closed with asbestos plugs to prevent excessive convection. The latter precaution gave satisfactory results and was adopted as part of the regular procedure. The correct position for the thermocouple was obtained from the distribution graph and readings taken at the central axis of the larger tubes and on the outside wall of the silica reactor because the size prevented insertion of a thermocouple pocket.

Liquids were fed to the reactor via a dropping funnel fitted with a pressure-balancing arm, low melting solids being liquified by electrical heating. Liquids and solids condensed together at the exit in water and air condensers. In specific pyrolyses reagent traps were included after the water condenser to remove volatile aldehydes and ketones (2:4-dinitrophenylhydrazine in 2N hydrochloric acid) and ketens (aniline, which reacts to give anilides). Finally the low boiling liquids were removed from the gases by a Drikold/acetone trap at -80°. The gas aspirator was maintained at atmospheric pressure and was filled with water covered by a thick layer of liquid paraffin to avoid solution of gas. Mercury manometers indicated pressure before and after the

FLOW PYROLYSIS APPARATUS.
(VERTICAL.)

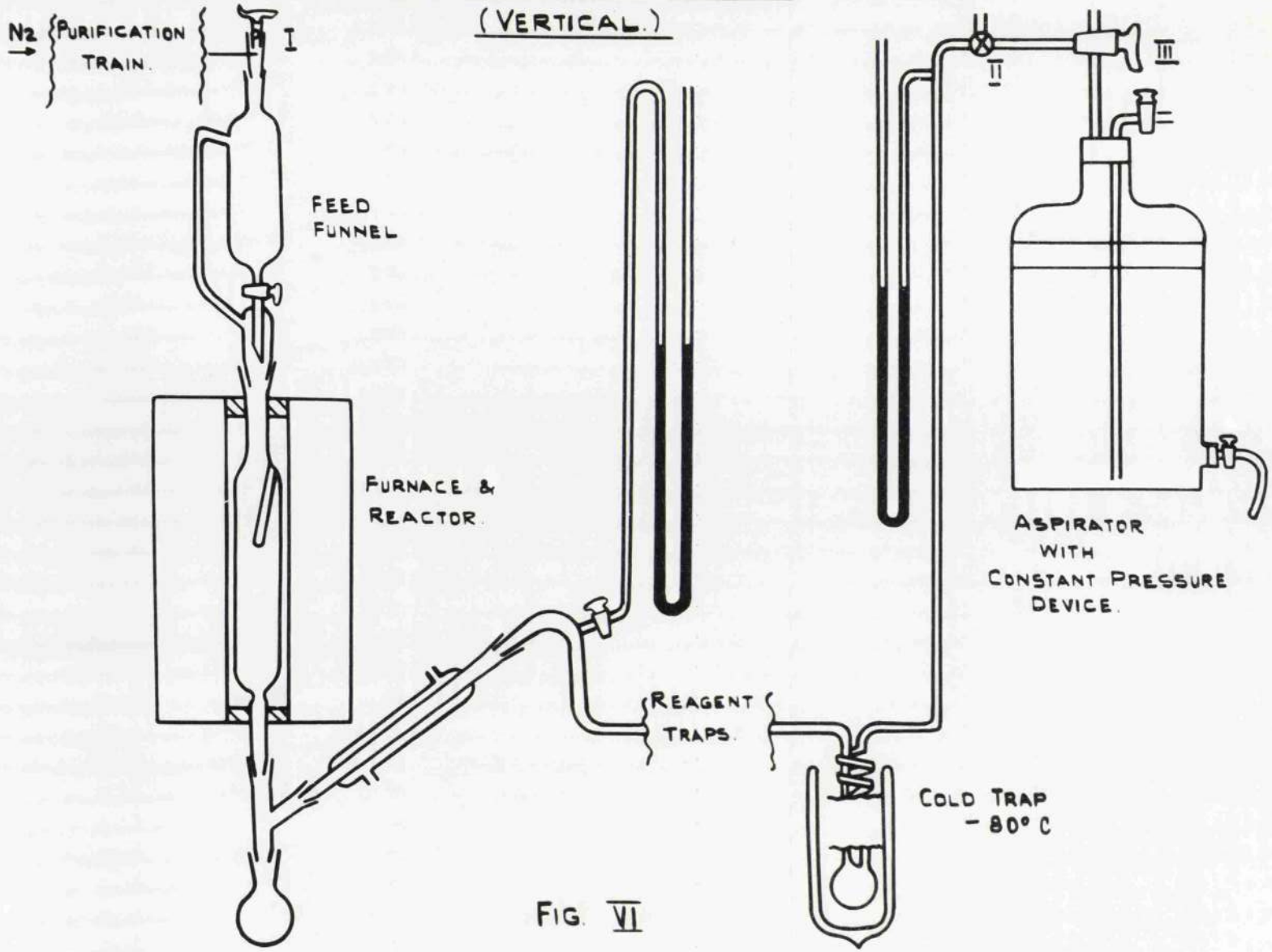
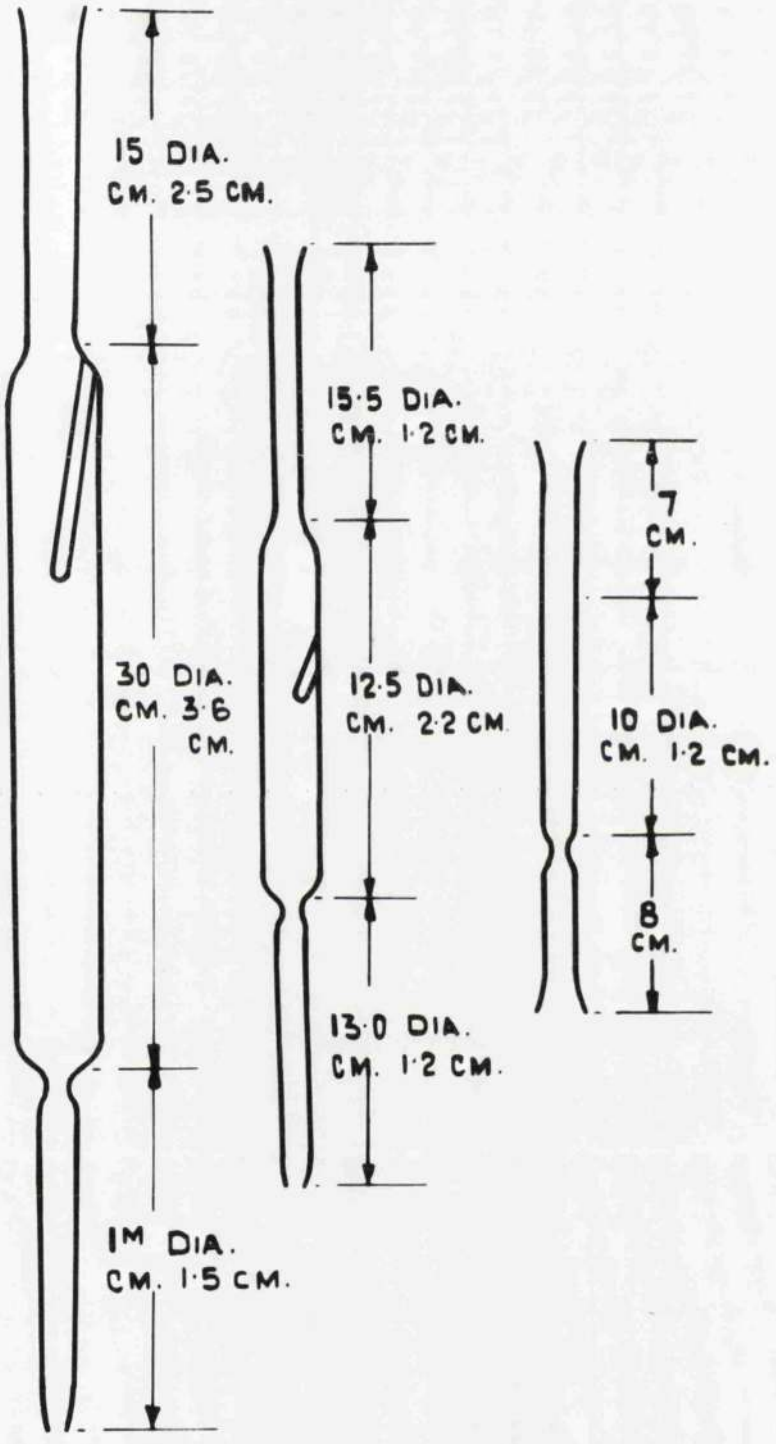


FIG. VI

FLOW PYROLYSIS REACTORS.



REACTION VOLUME:-

220 ML	20 ML	4 ML
A	B	C

FIG. VII

cold trap which was important as blocking of this receiver could cause pressure build-up in the reactor.

It was more convient to pyrolyse stable solids in the apparatus shown in Fig. VIII. The pyrolysand was melted in and distilled from a flask through a furnace inclined at approximately 10^{o} to horizontal, the receiving arrangement as before. The flow rate was less easily controlled than by the dropper but the problem of feeding a high melting solid was solved. Furnace B was suitable for the reaction vessel.

Oxygen was removed from the apparatus before commencement of a run by flushing with nitrogen and successive evacuations to 5 mm. pressure. Cooling of low boiling pyrolysands was necessary to prevent evaporation during evacuation.

Flow rate effects the extent of decomposition. The residence time was calculated from the Barton formula(112).

$$\text{Residence time} = \frac{3600 \times 273 \times V_c}{22400 \times (N_r + N_{N_2}) \times T}$$

V_c ..... contact volume

N_r ..... moles pyrolysand per hour

N_{N_2} ..... moles nitrogen per hour(in this case zero)

T ..... pyrolysis temperature, degrees absolute

Residence time is preferred to the previously used term, contact time, as there is no evidence that the material is

FLOW PYROLYSIS APPARATUS.
(HORIZONTAL.)

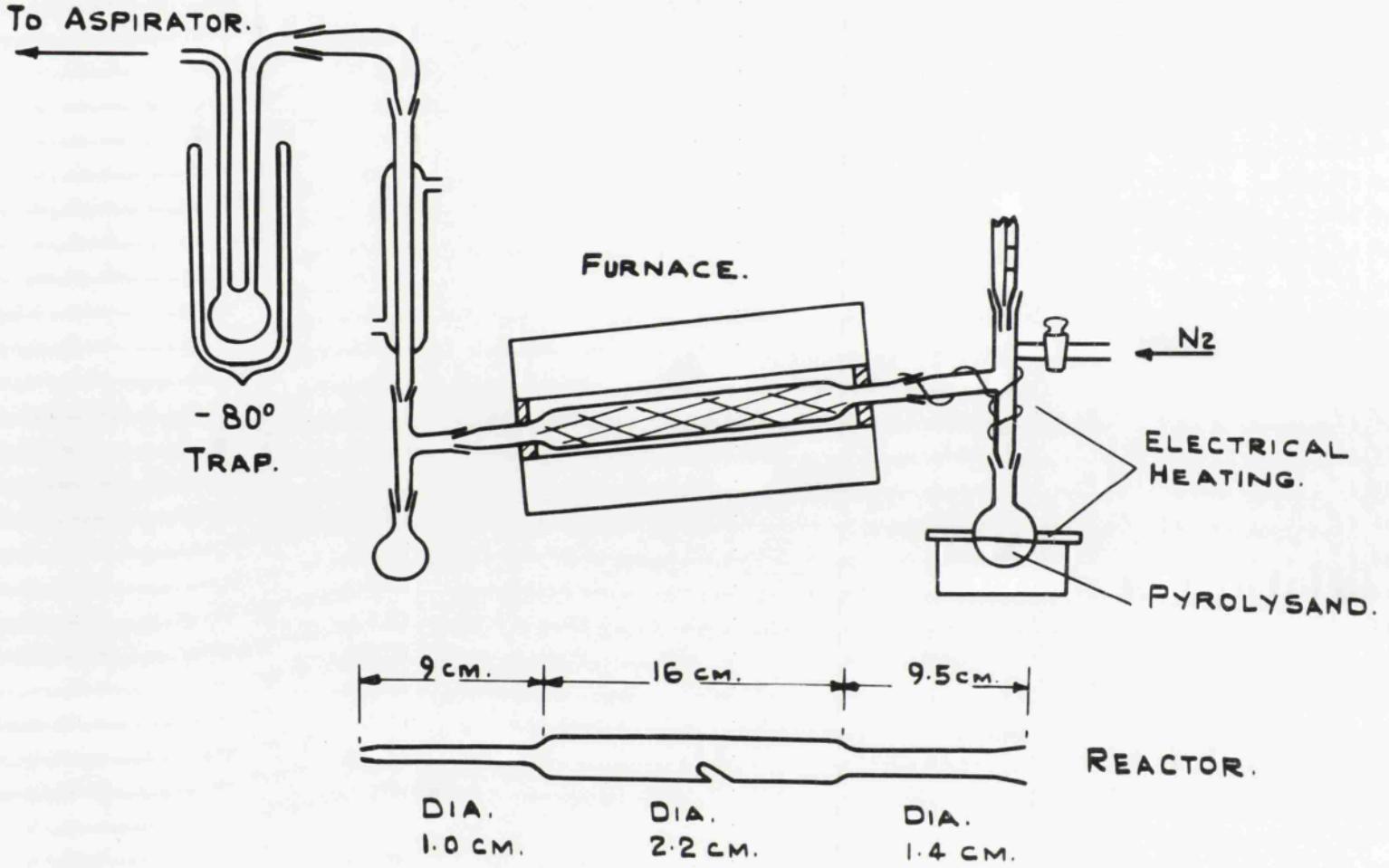


FIG. VIII

actually in contact with the packing. Comparison of the degrees of decomposition at the same residence time can be made irrespective of the different molecular weights.

Pyrolyses were invariably accompanied by some carbonisation of the reactor which was removed before each run by burning in a stream of air. Refluxing of concentrated nitric acid was sometimes necessary when carbonisation was heavy.

3.1.2. Chromatography.

a) Paper chromatography.

A method of separation of 2:4-dinitrophenylhydrazones of aldehydes and ketones, devised by Burton(113), was applied. Whatman No.1 paper was the support for a methanol-water-ethyl tartarate mixture in the ratio of 12:3:1. Elution with 2 - 3 % carbon tetrachloride in light petroleum ether separated the derivatives.

Circular papers held between glass plates and fed by a central wick gave fairly good separation but R_f values were not sufficiently reproducible for identification although a convient indication of more than one derivative was obtained. The usual tank method, using comparison standards, was satisfactory.

b) Column chromatography.

Separation of mixtures of 2:4-dinitrophenylhydrazones

on a column of bentonite/kieselghur(4:1) has been reported by Elvidge and Whalley(114). The solid was applied to the column in chloroform solution and eluted with chloroform/ethanol mixtures, increasing from 5 to 100 % alcohol. The dark colour of the column prevented easy detection of the bands, therefore the emergence was observed by measurement of the optical density of fractions with an Eel photometer. The method is extremely slow but had the advantage of allowing isolation of pure derivatives.

c) Gas-liquid chromatography.

This technique for separation of liquid mixtures has considerable advantages over convential distillation. Samples required are of the order of one or two drops and liquids of similar boiling points can be separated.

Martin and James devised the method in 1952 and much development has occurred since. An inert gas stream carries the vapourised sample through a column of absorbent liquid supported on an inactive solid e.g. kieselghur. Separation takes place by virtue of the differences of the partition coefficients of the materials between the gaseous and liquid phases. Column efficiencies of several thousand theoretical plates and numerous methods of detecting fractions have been reported(116).

In the present investigation two units have been employed. The first, built by Williams et al.(117), has twin

columns packed with silicone grease on kieselghur and hot-wire katharometer detectors, the whole being maintained at a constant temperature by a vapour jacket. One column separated the materials while the other served as a comparison reference. This unit was used for preliminary work at a column temperature of 100°.

A Griffin and George mark IIB model was used for the final analysis of pyrolysates. The single column was packed with silicone 301/kieselghur, heated by an air bath and had katharometer detectors. Temperature control was less exact than with a vapour jacket but this was compensated by the ease with which the working temperature could be altered. The lower temperatures obtainable were more suitable for analysis of the complex low-boiling mixtures.

Calculation of Standard Retention Volumes.

The method of calculation is designed to yield a value of retention volume which is independent of gas flow rate, weight of stationary liquid phase, inlet and oulet pressures. At a given working temperature the standard retention volume of a substance should be a constant for a particular stationary liquid phase.

Retention volume V_r = gas flow from column in unit time x time between the air peak and the centre of the zone.

V_r^o = retention volume corrected for pressure drop across the column.

$$V_g^o = V_r^o \text{ per g. stationary liquid phase}$$

$$V_r = R_t \times FR \times \frac{P_i \times T_w}{P_o \times T_a}$$

$$V_r^o = V_r \times \frac{3}{2} \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}$$

$$V_g^o = V_r^o/w$$

R_t = retention time

FR = nitrogen flow rate

P_i = inlet pressure

P_o = outlet pressure

T_w = column working temperature

T_a = atmospheric temperature

w = weight of stationary liquid phase

It was not possible to calculate the standard retention volumes for materials analysed on the Griffin and George column as the weight of liquid phase was not known. It could not be determined in the normal way, with a standard, as no data have been published for silicone 301. Comparison of retention volumes is sufficiently accurate for identification when the same column is used and a low working temperature limits loss of liquid phase.

Great care is essential in interpretating the results as two compounds may have very similar retention volumes. Use of different working temperatures resolved this difficulty.

Katharometer detectors give a response proportional to the thermal conductivity of the vapour and to the quantity present(117). For vapours having similar thermal conductivities the area under the peak gives an approximate measure of the

weight present. Trial estimations of synthetic mixtures on the Griffin and George column showed an error of ∓ 25 % and poor reproducibility. Accurate quantitative analysis was therefore not possible but a moderately good indication of relative proportions was obtained. Certain compounds gave very weak responses causing a false impression of the quantity and difficulty in detection. At the highest value of the variable sensitivity these could be identified but major fractions overloaded the detector. Runs were carried out at different sensitivities to complete analyses.

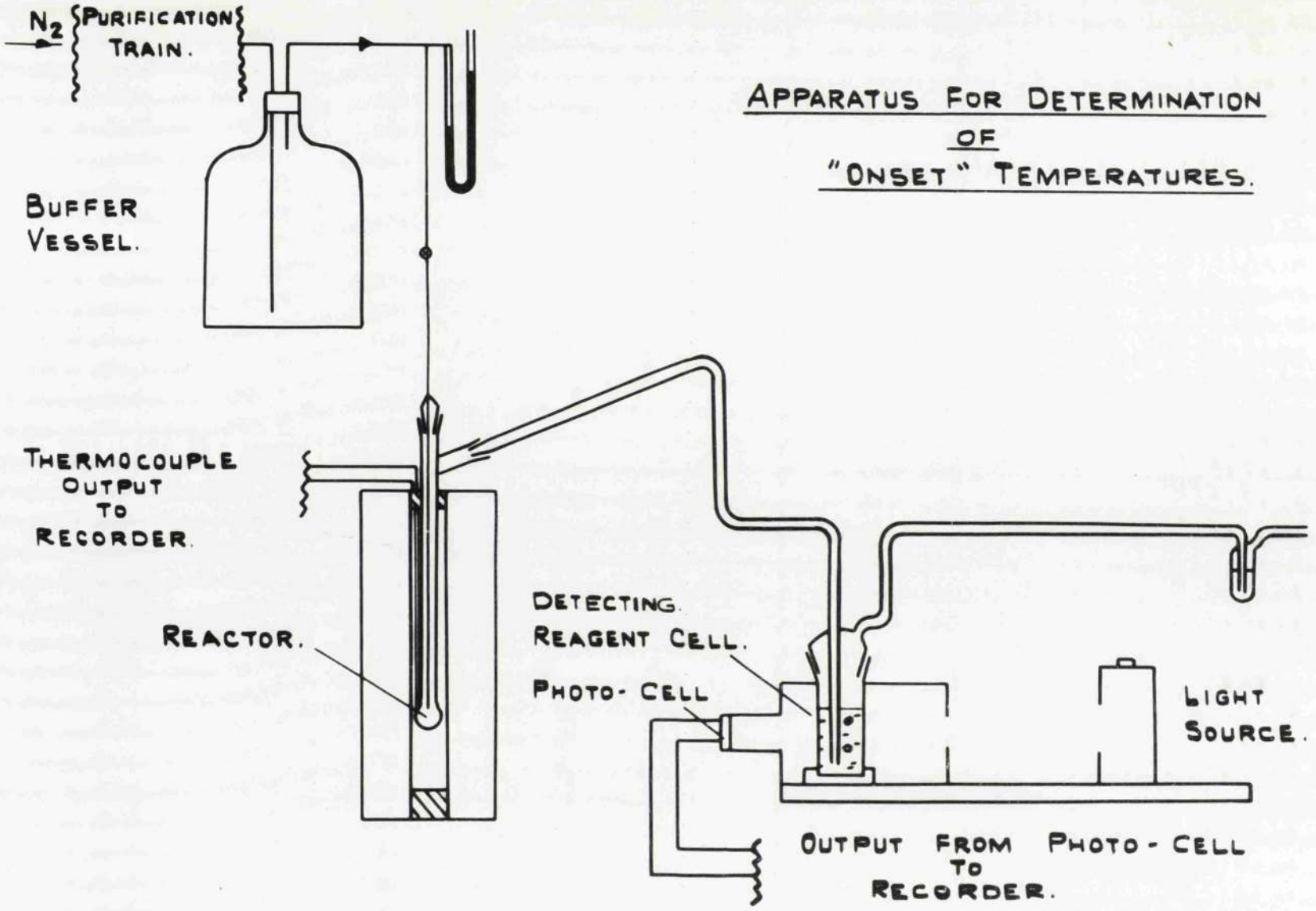
3.1.3. Infrared Spectrometer.

The double beam instrument has been described in detail by Brownlie(118). Closed and capilliary liquid cells were available also a 10 cm. gas cell.

Normally the spectrum of a pure fraction was obtained and compared with that of a pure standard which compensated for irregularities. The identity of olefins and saturated gases could be established from the spectrum of the total gas. Mixtures of low boiling esters were found to give unsatisfactory results owing to overlapping of peaks when traces of impurities were present.

3.1.4. Apparatus for Determination of 'Onset' Temperature.

The apparatus was devised and described in its original form by Mackinnon(48). Several modifications have been made but the basic principle remains the same. A continuous stream



APPARATUS FOR DETERMINATION OF "ONSET" TEMPERATURES.

FIG. IX

of nitrogen passes through a static reactor while the temperature is slowly raised, volatile products being carried to a detector. Evolution is indicated by change in optical density of a suitable reagent.

Fig. IX illustrates the apparatus. The reactor has a simple test-tube form with a small thermocouple pocket at the base. Nitrogen is admitted via an axial tube and a water condenser at the exit prevents carry-over. The output from the chromel-alumel couple is recorded on a 0 - 30 millivolt Kent recorder. The cylinder head was found to give fluctuations in the nitrogen pressure which interfered with optical density measurement. Insertion of a large buffer vessel and a needle valve gave the desired control.

The new detection unit, in which the thin glass reagent cell is placed, has light baffles, and the photocell is situated at the end of a cylindrical extension to exclude extraneous light. A beam of light focussed on the photocell, passes through the reagent. A Pye amplifier/ galvanometer records the output from the light cell

The gas stream enters the reagent via a dreschel head and the first evolution of a gaseous product alters the light absorption. Primary scissions which eliminate volatile products may be observed by an appropiate reagent solution.

Scission	Volatile product	Reagent	Sensitivity
A^1	olefin	Br_2/CCl_4	good
B^2	aldehyde	2:4-dinitrophenyl-hydrazine/2N HCl(119)	excellant
C^1	carbon monoxide	phosphomolybdic acid/ $PdCl_2$(120)	poor
C^2	carbon dioxide	aqueous $BaCl_2$	good

Although it is claimed that the threshold temperature for each route of a complex breakdown may be determined(48) no allowance can be made for secondary reactions. In the present work only the lowest temperature at which decompostion could be detected, the 'onset' temperature, is regarded as significant.

Boyd, using the modified apparatus, showed the reproducibiltiy of the determinations for gas rates of 15 - 20 ml. nitrogen per min. and varying sample size. The latter has a serious effect when a small reactor is used, quantities greater than 0.5 g. giving falsely high results. Rapid reflux in the 50 ml. reactor was thought to be the cause. Consistent readings were obtained with a larger vessel, reaction volume 175 ml., for samples up to 1.5 g.

The most important time lag is in the transference of the volatile product from the reactor to the detector. The dead-space was estimated to be 20 ml. and would be completely

swept once per minute with a gas flow of 20 ml./min. Heating at 1°/ min. gives a negligible error.

3.2. Analysis.

The gases were analysed by an absorption method while the combined liquid products were separated by fractionation. The -80° condensate was allowed to evaporate into an ice and a Drikold/acetone receiver. Chemical methods of identification were supplemented by infrared spectroscopy and in later stages of the work by gas/liquid chromatography. The latter was particularly useful in analysing pyrolysates from methyl esters which yielded complex azeotropes. For these mechanical separation was not possible and resolution of the infrared spectra was poor.

3.2.1. Gas Analysis.

A standard Hempel apparatus was supplemented with a potassium iodomercurate pipette for absorbing acetylene. The percentage combustible gas was determined by explosion with air and identification achieved by infrared.

3.2.2. Spot Tests.

a) Esters(122)

Esters when heated with hydroxylamine and sodium hydroxide give a sodium salt of hydroxamic acid. Acidification yields hydroxamic acid which forms a violet colour with ferric chloride.

The test solution is treated with equal volumes of saturated alcoholic hydroxylamine and aqueous sodium hydroxide. The mixture is warmed and on cooling, acidified with 2N hydrochloric acid. A violet colour on addition of a drop of ferric chloride confirms the presence of an ester.

b) Anhydrides(67)

This useful and sensitive test depends on the formation of an azlactone by the reagent, α-(p-nitrobenzoyl)-aminotoluic acid, with an anhydride. When a pyridine solution of the reagent is added to a similar solution of an anhydride a temporary blue or green colour develops. The reaction is general for all anhydrides with the exception of five and six-membered cyclic compounds.

c) Alcohols

(i) Alkali-alkyl xanthate test(120).

Primary and secondary alcohols can be detected by formation of an alkali-alkyl xanthate with sodium hydroxide and carbon disulphide, thus;

$$ROH + CS_2 + NaOH \rightarrow CS(OR)(SNa) + H_2O$$

Addition of a mineral acid solution of ammonium molybdate gives a violet colour.

Carbon disulphide and solid sodium hydroxide are mixed with the sample and after shaking ammonium molybdate and 2N sulphuric acid is added. The violet colour is seen more clearly if extracted with a few drops chloroform.

(ii) Vanadium oxinate test(123).

The reagent is a complex of vanadium with 8-hydroxyquinoline which is greenish-black in benzene solution. Alcohols give a red colour believed to result from the formation of an alcoholate. The reagent must be freshly prepared by mixing a solution containing vanadium with a 2.5 % solution of 8-hydroxyquinoline in 6 % acetic acid.

The test has the advantage of being sensitive for all alcohols and less affected by esters than the xanthate test. The colour change is moderately good but deteriorates on standing.

3.3. Preparation and Purification of Pyrolysands.

3.3.1. Esters of Dibasic Acids.

The normal methyl and ethyl esters were obtained from commercial sources or by simple esterification of the acid. Carbonate washing, drying over anhydrous magnesium sulphate and fractionation with a six inch Vigreux column yielded a pure pyrolysand. Two general methods were applied to the preparation of the hydrogen esters;

a) partial esterification of the acid(125) with limited quantity of alcohol in the presence of concentrated sulphuric acid,

b) reaction of the acid on the normal ester(126), refluxing of equimolar mixtures of the reactants giving good yields of the hydrogen ester.

Carbonate extraction of the distillate separated the hydrogen

ester. The extract was acidified and the ester taken up in ether. After drying, ether was removed under vacuum and the ester distilled at 5 - 15 mm. A pure product was obtained finally by a vacuum fractionation.

3.3.2. Monomeric Adipic Anhydride.

Polymeric adipic anhydride, formed by dehydration of the acid with acetic anhydride, may be decomposed to the monomer by heating under vacuum(127).

Adipic acid, one mole, was refluxed with three moles acetic anhydride for three hours. Vacuum removal of excess acetic anhydride was followed by reduction of pressure to 5 - 8 mm. and further heating. At 220° the pressure increased sharply to 14 mm. when the monomeric anhydride distilled at 100 - 125°. Crystals of adipic acid were centrifuged from the distillate and fractionation yielded the product, 97°/ 1 - 3 mm.

Analysis: Found 56.1 % C; 6.4 % H; 37.5 % O.

Calc. 56.25 % C; 6.28 % H; 37.47 % O.

Molecular weight: Found, in benzene, 130.2.

Calc. 128.0.

3.3.3. Acrylic Anhydride.

Acryloyl chloride and sodium acrylate, in equimolar quantities, react to form acrylic anhydride(128).

The chloride was prepared simply by warming acrylic acid with benzoyl chloride. The product distilled at 73 - 81° and redistilled at 75 - 76°. It was added dropwise to sodium acrylate, moistened with a little liquid paraffin, with continuous stirring, the temperature being maintained below 20°. The mixture was refluxed for half an hour and then distilled at 38 mm., the 97 - 103° fraction being collected. Yields from several preparations were combined, three fractionations giving pure acrylic anhydride, 97°/38 mm. It is a colourless highly lachrymatory liquid which polymerises with ease.

Analysis: Found 56.7 % C; 4.8 % H; 38.5 % O.

Calc. 57.1 % C; 4.76 % H; 38.14 % O.

A second method was devised for preparation of acrylic anhydride. The acid was dehydrated by refluxing with three moles acetic anhydride for six to eight hours, addition of 10 - 15 % hydroquinone preventing polymerisation. Yields were low but recovery of the acid was possible and the overall yield was comparable to the previous method, 5 - 15 %. Purification was as above.

3.3.4. α-Methylacrylic Anhydride.

The action of thionyl chloride on potassium α-methylacrylate, at moderate temperature, gives α-methylacrylic anhydride(129).

Thionyl chloride, 65 g., in 250 g. dry petroleum ether was added to 50 g. dry potassium α-methylacrylate and the

temperature held at 55 - 60° for six hours. Filtration was followed by vacuum distillation, the fraction 82 - 86°/11 mm. being collected. The combined yields were fractionated twice, α-methylacrylic anhydride distilling finally at 84°/11 mm. The colourless liquid polymerises with great ease.

Analysis: Found 62.55 % C; 6.7 % H; 30.75 % O.

Calc. 62.3 % C; 6.5 % H; 31.2 % O.

Dehydration of α-methylacrylic acid with acetic anhydride in presence of hydroquinone gave slightly improved yields, 8 - 12 %.

A mixture of one mole α-methylacrylic acid, three moles acetic anhydride and 10 - 15 % hydroquinone was heated on a steam bath for 10 to 12 hours, higher temperatures giving extensive polymerisation. The crude material was combined with product from the above preparation.

3.3.5. Propiolaldehyde.

Controlled oxidation of propargyl alcohol at room temperature yields propiolaldehyde(130).

360 ml. of a 33 % aqueous solution of the alcohol was placed in an ice cooled flask. Nitrogen was admitted to the system via a capilliary immersed in the liquid and the pressure was maintained at 40 -60 mm. A cooled solution of 135 ml. concentrated sulphuric acid in 200 ml. water was added. Chromium trioxide, 210 g. in 135 ml. concentrated sulphuric acid and 400 ml. water, was dropped into the flask over three

hours. Propiolaldehyde was removed as it was formed and condensed at -80°. It is a colourless, lachrymatory liquid boiling at 49 - 50°.

3.4. Experimental Results.

Results have been stated in tabular form, the numerials assigned to the pyrolysands, Table 1, Section 2, being used. Tables 6 and 7 contain respectively distillation data and summaries of qualitative analyses by conventional methods while retention volumes obtained by gas-liquid chromatography are listed in Table 9.

Abbreviations:

t ... trace

L ... light

M ... moderate

H ... heavy

P ... derivative obtained

n ... no derivative

- ... trap omitted

Table 4 - Flow Pyrolysis Conditions and Yields.

Run No.	1	2	3	4	5	6	7	8	9	10	11	12
Pyrolysand	I	I	I	I	I	II	II	III	IV	V	V	V
Temperature °C.	5000	500	500	500	500	500	500	500	500	500	500	500
Reactor	A	A	A	A	A	A	A	A	A	A	A	A
Wt. Pyrolysed g.	40	40	23	75	100	40	38	20	40	40	40	40
Feed Rate g./min.	.332	.421	.23	.169	.589	.50	.60	.37	.385	1.0	1.3	.25
Residence Time	138	109	200	274	79	69	54	85	69	53	44	240
% Decomposition	89	85	92	96	89	97	98	58	55	93	93	96
Carbonisation	M.	M	L	M	H	M	M	L	L	M	M	M
Mass Balance	95	91	91	95	91	92	89	97	95	94	91	91
Products:												
Liquids g.	13.7	13.0	6.9	25.0	30.4	9.0	7.2	6.3	4.5	13.9	12.0	18.3
Solids g.	4.58	5.5	2.5	5.5	19.5	13.2	14.5	7.1	18.0	6.3	7.7	3.2
Gas litres NTP.	15.1	13.0	8.27	30.7	30.9	10.4	11.7	3.49	10.5	10.6	12.2	12.9
2:4-DNP trap	-	-	P	-	-	-	P	-	P	-	P	-
Aniline trap	-	-	-	n	-	-	-	-	-	-	-	n

Abbreviations:

t	... trace
L	... light
M	... moderate
H	... heavy
P	... derivative obtained
n	... no derivative
-	... trap omitted

Table 4 (cont.) - Flow Pyrolysis Conditions and Yields.

Run No.	13	14	15	16	17	18	19	20	21	22	23	24
Pyrolysand	VI	VII	VIII	VIII	VIII	IX	X	X	X	X	XI	XI
Temperature °C.	500	500	500	500	500	500	500	500	500	500	500	500
Reactor	H	B	A	A	A	H	A	A	A	A	A	A
Wt. Pyrolysed g.	22.5	8.6	40	50	50	19.25	50	40	40	30	50	40
Feed Rate g./min.	.225	.108	.333	.528	.333	.226	.667	.475	.525	.20	.37	.381
Residence Time	66	22.5	205	129	205	55	58	80	73	193	123	121
% Decomposition	80	95	97	96	98	90	18	23.5	20.7	36.3	30	31
Carbonisation	L	t	M	M	M	L	t	t	t	t	t	t
Mass Balance	91	98	-	97	90	95	96	97	100	96	98	98
Products:												
Liquids g.	10.9	6.7	4.8	4.8	5.6	5.4	41.3	33.2	34.4	24.7	40.1	29.6
Solids g.	3.4	-	20	27	19	6.4	-	-	-	-	-	-
Gas litres NTP.	3.27	0.96	10.9	13.5	16.0	3.4	5.61	4.2	3.71	3.45	7.47	7.16
2:4-DNP trap	-	-	-	P	-	-	P	-	-	-	P	-
Aniline trap	-	-	-	-	n	-	-	n	-	-	-	n

Abbreviations:

t	... trace
L	... light
M	... moderate
H	... heavy
P	... derivative obtained
n	... no derivative
-	... trap omitted

Table 4 (cont.) - Flow Pyrolysis Conditions and Yields.

Run No.	25	26	27	28	29	30	31	32	33	34	35	36
Pyrolysand	XI	XI	XII	XII	XIII	XIII	XIV	XV	XVI	XVII	XVII	XVIII
Temperature °C.	500	500	500	500	500	500	500	500	500	500	500	540
Reactor	A	A	A	A	A	A	C	A	A	A	A	C
Wt. Pyrolysed g.	40	29	37.3	30	18.8	30.3	15.3	30	40	40	30	8.2
Feed Rate g./min.	.34	.34	.429	.259	.094	.333	.133	.261	.186	.222	.173	.126
Residence Time	138	135	98.5	163	680	185	31.5	78.1	188	119	153	4.9
% Decomposition	33.2	24.7	23	24.9	41.5	26	12.2	17	52.4	54	68	47
Carbonisation	t	t	t	t	t	t	t	t	t	t	t	t
Mass Balance	100	99	99	97	97	95	97	96	97	93.3	92.4	92
Products:												
Liquids g.	30.8	25.3	26.3	24.2	13.1	24.3	13.7	23.4	28.8	30.6	19.7	5.44
Solids g.	t	t	-	-	t	0.2	-	-	-	-	-	-
Gas litres NTP.	6.14	2.55	7.96	3.98	3.33	3.14	0.79	4.67	6.69	5.01	7.11	1.15
2:4-DNP trap	-	-	-	-	P	-	-	-	-	P	-	-
Aniline trap	-	-	-	n	-	n	-	-	-	-	n	-

Abbreviations:

t	... trace
L	... light
M	... moderate
H	... heavy
P	... derivative obtained
n	... no derivative
-	... trap omitted

Table 4 (cont.) - Flow Pyrolysis Conditions and Yields.

Run No.	37	38	39	40	41	42	43	44	45	46	47	48
Pyrolysand	XIX	X ≠	IV	IV	XX	XX	XX	XXI	XXI	XXI	XXII	XXII
Temperature °C.	540	500	500	570	500	350	430	500	600	550	500	500
Reactor	C	A	A	H	A	H	H	C	C	C	A	A
Wt. Pyrolysed g.	6.2	22	80	24.8	20	53.8	37	8.2	3.0	5.4	41.5	56
Feed Rate g./min.	.102	.16	.485	.291	.133	.346	.265	.092	.033	.05	.213	.465
Residence Time	5.1	43	56.5	129.5	195	14.0	14.5	4.7	11.3	8.1	127	58
% Decomposition	42	13	49	80	50	-	8.9	-	95	58	46.7	35
Carbonisation	L	L	M	M	M	t	L	t	M	t	M	M
Mass Balance	98	98	93	98	99	98	98	95	98	96	95	99
Products:												
Liquids g.	5.1	20.3	13.3	6.6	-	-	-	(	t	(	31.5	50.2
Solid g.	-	-	43	5.2	10	52	33.7	(7.8 (	1.4	(4.0 (	-	-
Gas litres NTP.	0.96	1.03	11.5	6.8	8.0	-	1.86	-	1.17	0.89	4.3	3.77
2:4-DNP trap	-	-	-	-	-	n	-	-	-	-	-	P
Aniline trap	-	-	-	n	-	-	n	-	-	-	P	-

≠ containing 5 % hydroquinone

Abbreviations:

t	... trace
L	... light
M	... moderate
H	... heavy
P	... derivative obtained
n	.... no derivative
-	... trap omitted

Table 4 (cont.) - Flow Pyrolysis Conditions and Yields.

Run No.	49	50	51	52	53
Pyrolysand	XXIII	XXIII	XXIV	XXV	XXV
Temperature °C	500	500	500	500	500
Reactor	B	B	B	B	B
Wt. Pyrolysed g.	15	14.5	11.4	12.65	16.6
Feed Rate g./min.	.15	.415	.153	.633	.216
Residence Time	24	6.4	6.0	6.4	24
% Decomposition	88	73	50	45	56
Carbonisation	L	L	H	L	L
Mass Balance	97	99	77.6	98	98.5
Products:					
Liquid g.	7.3	9.5	6.0	10.4	10.3
Solid g.	-	-	-	-	-
Gas litres NTP.	4.66	3.84	2.3	1.54	3.39
2:4-DNP trap	-	-	-	P	-
Aniline trap	-	n	-	-	n

Abbreviations:

t	... trace (infrared)
-	... not present
x	... not analysed
n	... no gaseous product

Table 5 - Absorption Analyses of Gaseous Pyrolysates.

Run No.	1	2	3	4	5	6	7	8	9
CO_2	17.5	15.78	17.5	16.6	12.6	9.76	13.85	37.7	29.2
C_2H_2	-	-	-	-	t	-	-	t	x
Olefin	56.2	62.55	59.1	61.2	66.5	59.0	52.3	17.8	10.65
CO	20.0	19.82	20.2	20.8	17.63	29.0	29.6	44.5	60.2
Sat.H/C.	3.68	1.74	3.23	1.38	3.26	2.28	4.39	-	-
H_2	-	-	-	-	-	-	-	-	-

Run No.	10	11	12	13	14	15	16	17	18
CO_2	25.1	20.8	28.3	86.1	83.2	10.0	12.6	14.1	68.0
C_2H_2	t	t	1.5	-	-	1.4	t	1.0	-
Olefin	64.7	68.4	57.0	5.76	6.75	66.5	69.9	64.9	10.2
CO	6.2	7.0	6.8	8.17	10.4	10.9	9.4	14.3	21.8
Sat.H/C	4.2	3.76	6.4	-	-	9.6	9.1	5.7	-
H_2	-	-	-	-	-	-	-	-	-

Run No.	19	20	21	22	23	24	25	26	27
CO_2	26.2	28.0	29.2	18.9	18.8	19.5	18.2	17.7	12.0
C_2H_2	t	t	t	t	t	t	t	t	t
Olefin	9.5	8.5	9.9	8.8	17.6	19.0	19.3	19.2	13.8
CO	25.4	22.8	24.0	28.4	44.6	44.1	45.8	48.3	54.5
Sat.H/C	15.4	22.3	20.4	17.5	12.9	12.6	12.1	12.4	13.3
H_2	23.5	18.4	16.6	26.3	6.1	4.8	4.6	2.5	6.4

Abbreviations:

t	... trace (infrared)
-	... not present
x	... not analysed
n	... no gaseous product

Table 5 (cont.) - Absorption Analyses of Gaseous Pyrolysates.

Run No.	28	29	30	31	32	33	34	35	36
CO_2	15.0	13.7	37.8	16.9	6.1	4.5	2.7	3.0	6.4
C_2H_2	t	1.8	1.8	t ≠	-	t	1.3	1.5	t
Olefin	11.5	21.6	5.6	12.7	8.4	8.1	3.6	4.0	38.3
CO	52.5	36.9	35.6	49.5	50.0	77.6	81.8	91.5	22.2
Sat.H/C.	15.6	10.5	14.0	6.7	21.3	0.8	1.2	x	26.0
H_2	5.3	16.4	5.2	12.2	14.2	10.0	9.4	x	7.1

Run No.	37	38	39	40	41	42	43	44	45
CO_2	6.6	24.8	16.2	28.2	33.1	n	52.1	n	30.8
C_2H_2	t	t	t	0.2	32.3	n	19.6	n	0.8
Olefin	34.0	16.3	10.5	13.6	0.39	n	t	n	17.4
CO	22.8	37.4	73.4	58.0	34.21	n	28.3	n	51.0
Sat.H/C.	22.8	9.8	-	-	-	n	-	n	-
H_2	9.0	11.75	-	-	-	n	-	n	-

Run No.	46	47	48	49	50	51	52	53
CO_2	18.7	47.5	36.9	15.4	13.8	4.2	26.5	34.7
C_2H_2	t	t	t	18.1	25.8	7.8	.87 ≠	t ≠
Olefin	18.4	13.6	13.2	8.38	5.4	4.0	11.1	9.1
CO	62.9	38.9	42.0	58.12	55.0	83.9	61.7	56.2
Sat.H/C.	-	x	7.9	-	-	-	-	-
H_2	-	-	-	-	-	-	-	-

≠ methylacetylene

Table 6 - Fractionation of Liquid Pyrolysates.

Run No.	Pyrol[nd].		Fraction i	ii	iii	iv	v	vi	vii	viii	Residue
1	I	°C.	50-70	70-95	95-101	139-143	100-105 /15 mm.	141-145 /15 mm.			
		g.	0.3	1.3	1.6	2.1	4.2	0.4			2.6 s
2	I	°C. /80 mm.	-40	40-44	44-55	75-82	120-126	170-175			
		g.	0.5	1.4	2.0	2.6	5.2	0.3			1.5 s
3	I	°C.	50-70	70-100	100-102	139-143	215-219	-			
		g.	0.2	0.8	1.0	1.3	1.7				1.7
4	I	°C.	50-70	70-98	98-100	69-72 /60 mm.	70-75 /7 mm.	123-127 /7 mm.			
		g.	0.7	1.9	3.1	5.2	6.8	0.2			5.1 s
5	I	°C.	50-70	70-98	98-101	138-140	109-113 /20 mm.	149-151 /20 mm.			
		g.	0.3	3.9	4.0	6.1	10.6	0.6			3.6 s
6	II	°C.	79-98	98-100	137-140	102-105 /15 mm.	140-147 /15 mm.				
		g.	1.6	2.3	2.4	0.9	t				0.5 s
7	II	°C.	75-98	98-101	138-143	70-77 /9 mm.	123-127 /9 mm.				
		g.	1.2	1.7	2.0	0.4	0.1				0.5
8	III	°C.	-60	96-100	134-139						
		g.	t	1.8	0.9						2.9 s
9	IV	°C.	-65	138-140							
		g.	t	4.2							0.2 s

Table 6 (cont.) - Fractionation of Liquid Pyrolysates.

Run No.	Pyrolnd.		Fraction i	ii	iii	iv	v	vi	vii	viii	Residue
10	V	°C.	80-92	92-98	98-103	128-131	145-151	178-185	130-134 /15 mm.	168-174 /15 mm.	
		g.	0.3	2.7	0.5	4.5	0.1	0.2	3.3	0.3	1.8 s
11	V	°C.	80-92	92-98-	98-104	126-131	146-151	173-183	245-248	-	
		g.	0.8	1.8	2.2	2.3	0.2	t	3.5		1.6 s
12	V	°C.	-	86-97	97-104	126-132	143-149	72-81 /10 mm.	118-123 /10 mm.	170-175 /10 mm.	
		g.		1.0	3.2	8.5	0.3	0.3	3.6	0.2	1.3 s
13	VI	°C.	95-99	127-131	178-184						
		g.	6.3	4.5	0.2						3.6 s
14	VII	°C.	128-132	180-185							
		g.	5.8	0.2							t
15	VIII	°C.	-36	66-72	88-99	118-125	185-189	136-139 /20 mm.	189-193 /20 mm.	-	
		g.	1.0	0.7	0.7	0.2	0.4	0.4	1.1		0.4 s
16	VIII	°C.	-34	66-72	87-98	119-125	77-81 /10 mm.	129-135 /10 mm.	175-180 /10 mm.	191-195 /10 mm.	
		g.	0.6	0.4	0.5	0.1	0.3	0.4	2.1	0.2	0.3 s
17	VIII	°C.	x	x	x	x	77-82 /10 mm.	129-135 /10 mm.	176-179 /10 mm.	-	
		g.	-	3.1	-		0.3	0.3	1.1		0.7 s

Table 6 (cont.) - Fractionation of Liquid Pyrolysates.

Run No.	Pyrolnd.		i	ii	iii	Res.
18	IX	°C.	60-65	98-100	-	
		g.	0.1	3.3		1.7 s
39	IV	°C.	-	65-72 /55 mm.	-	
		g.		12.4		0.6 s
40	IV	°C.	45-55	52-54 /34 mm.	-	
		g.	t	6.1		0.4 s
45	XXI	°C.	69-98	162-166	-	
		g.	t	0.7		0.2 s
46	XXI	°C.	65-94	161-166	-	
		g.	0.1	0.9		1.7 s
47	XXII	°C.	45-55	117-121	139-143	
		g.	t	8.7	21.0	1.7 l
48	XXII	°C.	48-56	117-120	139-142	
		g.	0.1	11.9	34.5	1.2 l
49	XXIII	°C.	-25 /150 mm.	79-86 /150 mm.	69-73 /12 mm.	
		g.	t	7.1	1.1	0.9 s
50	XXIII	°C.	-	45-49 /10 mm.	68-71 /10 mm.	
		g.		4.8	3.2	0.9 s
51	XXIV	°C.	53-57	-	-	
		g.	5.4			0.4 s
52	XXV	°C.	-35 /170 mm.	96-110 /170 mm.	99-103 /11 mm.	
		g.	0.2	2.9	5.9	1.1 s
53	XXV	°C.	-25 /7 mm.	56-63 /7 mm.	72-76 /7 mm.	
		g.	0.4	2.7	5.0	1.0 s

Table 7 - Analysis of Liquid/Solid Pyrolysates.

Run No.	Pyrolnd.	Fract.	Identification
1-5.	I	cold trap liquid	Aldehyde; column chromatography of crude DNP derivative gave two fractions, a) acetaldehyde, mp 164-166° mixed mp 165-166°; b) propionaldehyde, mp 154-156° mixed mp 155-156°.
		i	Alcohol, aldehyde; a) DNP derivative mp 155-156° mixed with propionaldehyde derivative mp 155-156°, b) 3:5-dinitrobenzoate mp 91-93° mixed with ethyl ester mp 91-93°.
		ii & iii	Alcohol, water and ester; a) water confirmed by anhydrous copper sulphate and Fischer reagent, b) excess sodium acetate added, distilled. Fraction 78-80°, alcohol, 3:5-dinitrobenzoate mp 90-92° mixed with ethyl ester mp 92-93° and fraction 98-100°, ethyl propionate identified by infrared and hydrolysis to propionic acid and ethanol.
		iv	Unsaturation, acid; acrylic acid identified as the dibromo derivative, mp 61-64 mixed mp 63-64°. The acrylic acid was polymerised with benzoyl peroxide and the unchanged liquid distilled at 139-141°, propionic acid by infrared and p-nitrobenzyl ester mp 28-30° mixed 28-30°.
		v	Ester; ethyl succinate by infrared.
		vi	Acid, ester; heating yielded succinic acid and ethyl succinate. Ethyl hydrogen succinate confirmed by infrared.
		solid	Acid; extraction with hot chloroform, residue was succinic acid mp 185° mixed mp 185°. Needle crystals from extract gave mp 119° mixed with succinic anhydride mp 119°.
6,7.	II	cold trap liquid	Aldehyde; acetaldehyde, DNP derivative mp 160-163° mixed mp 162.5-164°.

Table 7 (cont.) - Analysis of Liquid/Solid Pyrolysates.

Run No.	Pyrol nd.	Fract.	Identification
6,7.	II	i & ii	Alcohol, water; anhydrous copper sulphate confirmed water. Sodium acetate was added and the alcohol distilled 77-80°. Shown to be ethanol, 3:5-dinitrobenzoate mp 89-92° mixed mp 90-92°.
		iii	Unsaturation, acid; acrylic acid, infrared and the dibromo derivative mp 61-63° mixed mp 62-63°. Acrylic acid was polymerised and a liquid distilled from the solid, 137-140°. Infrared and p-nitrobenzyl ester, mp 27-29° mixed mp 28-30°, confirmed propionic acid.
		iv	Ester; ethyl succinate by infrared and refluxing with ethanolamine to form N:N-di-β-hydroxyamide mp 154-156° mixed mp 155-156°.
		v	Acid, ester; unchanged ethyl hydrogen succinate, infrared.
		solid	Acid; extraction with hot chloroform, residue - succinic acid mp 184° mixed mp 185°. Succinic anhydride crystallised mp 119° mixed mp 119°.
8	III	cold trap & DNP trap	Aldehyde; paper chromatography showed a single DNP derivative of acrolein, mp 160-163° mixed mp 161-163°.
		i	Acrolein confirmed as above.
		ii	Water confirmed by anhydrous copper sulphate and Fischer reagent.
		iii	Unsaturation, acid; Acrylic acid, infrared and α:β-dibromopropionic acid mp 59-62° mixed mp 60-62°.
9	IV	cold trap & i	Aldehyde; Acrolein, DNP derivative mp 160-163° mixed mp 160-163°.

Table 7 (cont.) - Analysis of Liquid/Solid Pyrolysates.

Run No.	Pyrolnd.	Fract.	Identification
9.	IV	ii	Unsaturation, acid; acrylic acid by infrared and dibromo derivative mp 58-62° mixed mp 60-62°.
10, 11,12.	V	cold trap	Distilled from a water bath. Condensate in ice cooled receiver was aldehydic, DNP derivative mp 160-163° mixed with acetaldehyde derivative mp 163-164°. Condensate in trap at - 80° contained n-butane and n-but-1-ene, confirmed by infrared.
		i	Alcohol, water; anhydrous copper sulphate showed water present. Sodium acetate was added and alcohol distilled 77-80°. 3:5-dinitrobenzoate had mp 91-93° mixed with ethyl ester mp 92-93°, ethanol confirmed.
		ii & iii	Water, ester, carbonyl; water as above. DNP derivative mp 94-96° mixed with n-valeraldehyde derivative mp 95-96°. The azeotrope was broken down by addition of sodium acetate. Distillation gave two fractions, 105-110°, mainly water and 118-130°, ethyl n-valerate confirmed by infrared and hydrolysis.
		iv	Water, carbonyl; two layers - lower water positive reaction with Fischer reagent. Upper layer cyclopentanone, DNP derivative mp 138-139° mixed mp 139-140°.
		v	Ester; confirmed to be ethyl n-valerate by infrared.
		vi	Unsaturation, acid; allylacetic acid by infrared and dibromo derivative mp 52-55° mixed mp 52-55°. Combined fractions brominated with Br_2/CS_2. The solvent removed under vacuum and n-valeric acid distilled, p-bromophenacyl ester mp 62-64° and mixed mp 62-64°.
		vii	Ester; ethyl adipate confirmed by infrared.
		viii	Acid, ester; ethyl hydrogen adipate - infrared and disproportionation to adipic acid and ethyl succinate. mp of the ester 25-28° mixed mp 26-28°

Table 7 (cont.) - Analysis of Liquid/Solid Pyrolysates.

Run No.	Pyrol^nd.	Fract.	Identification
10, 11,12.	V	solid	Acid; adipic acid mp 146-148°, mixed mp 148-149°. No anhydride detected with Davidson and Newman colour test(67).
13	VI	cold trap	n-but-1-ene by infrared.
		i	Water, carbonyl; anhydrous copper sulphate and Fischer reagent confirmed water. DNP derivative mp 136-138°, mixed with cyclopentanone derivative mp 137-139°.
		ii	Water, carbonyl; water and cyclopentanone identified as above.
		iii	Unsaturation, acid; infrared showed allylacetic acid.
14	VII	cold trap	n-but-1-ene identified by infrared.
		i	Carbonyl; cyclopentanone, DNP derivative mp 137-138°, mixed mp 137-138°.
		ii	Unsaturation, acid; Allylacetic acid confirmed by infrared.
15, 16,17.	VIII	cold trap	Liquid combined with total pyrolysate. A trace condensed in -80° trap during distillation. Infrared gave no definate information.
		i	Carbonyl; acetaldehyde, DNP derivative mp 162-164°, mixed mp 163-165°.
		ii	Unsaturation; Infrared indicated n-hexane and n-hex-1-ene.
		iii	Water, ester; water shown by Fischer reagent Ethyl pelargonate, which forms azeotrope with water, suspected.
		iv	n-octane identified by infrared.

Table 7 (cont.) - Analysis of Liquid/Solid Pyrolysates.

Run No.	Pyrol nd.	Fract.	Identification
15, 16,17.	VIII	v	Carbonyl; pelargonaldehyde DNP derivative mp 90-93°, mixed mp 91-93°.
		vi	Acid; pelargonic acid confirmed by infrared and p-bromophenacyl ester mp 61-65°, mixed mp 63-65°.
		vii	Ester; unchanged ethyl sebacate confirmed by infrared.
		viii	Acid,ester; disproportionation to sebacic acid and ethyl sebacate and infrared confirmed ethyl hydrogen sebacate.
		solid	Acid; sebacic acid mp 131-132°, mixed mp 131-132°. No anhydride found.
18.	IX	cold trap & i	n-hexane confirmed by infrared.
		ii	water shown by Fischer reagent.
39, 40.	IV	cold trap & i	Carbonyl; acrolein, DNP derivative mp 160-163°, mixed mp 160-163°.
		ii	Unsaturation, acid; dibromo derivative, mp 58-62° and mixed mp 60-62°, and infrared confirmed acrylic acid.
		solid	Succinic anhydride mp 118°, mixed mp 119°.
45, 46.	XXI	cold trap & i	Carbonyl, unsaturated gas; paper chromatography of DNP derivative showed α-methylacrolein and crotonaldehyde. Propene identified by infrared.
		ii	Acid, unsaturation; α-methylacrylic acid by infrared.
		solid	Methylsuccinic anhydride mp and mixed mp 29-31°.

Table 7 (cont.) - Analysis of Liquid/Solid Pyrolysates.

Run No.	Pyrol nd.	Fract.	Identification
47, 48.	XXII	cold trap	Unsaturation, carbonyl; keten identified by formation of acetanilide mp 111-113°, mixed mp 112-113°. Two carbonyl compounds shown to be acetaldehyde and acetone by paper chromatography.
		i	Carbonyl; acetone containing a trace of acetaldehyde by paper chromatography of DNP derivatives.
		iii	Acetic anhydride, anilide mp 109-111°, mixed mp 110-112°.
49, 50.	XXIII	cold trap & i	Carbonyl; acrolein, DNP derivative mp 158-163°, mixed mp 160-163°.
		ii	Unsaturation, acid; Acrylic acid, dibromo derivative mp 59-61, mixed mp 59-61°
		iii	Acrylic anhydride by infrared.
		solid	Polymeric; assumed to be polymeric acrylic anhydride.
52, 53.	XXV	cold trap	Unsaturation, carbonyl; methylacetylene identified by infrared. Paper chromatography confirmed the DNP derivative of α-methyl-acrolein.
		i	Carbonyl; α-methylacrolein, DNP derivative mp181-184°, mixed mp 182-185°.
		ii	Acid, unsaturation; α-methylacrylic acid by infrared.
		iii	α-Methylacrylic anhydride confirmed by infrared
		solid	Polymeric; assumed to be polymeric α-methylacrylic anhydride.

Abbreviations: P ... a principal olefinic or saturated gas

m ... a minor " " " "

t ... a trace " " " "

Table 8 - Qualitative Infrared Analysis of Gases.

Run No.	Pyrolysand	Gas Identified	Relative Quantity
1,2,3.	I	methane	P
		ethane	P
10,11,12.	V	methane	P
		n-butane	t
		ethylene	P
		n-but-1-ene	t
13	VI	ethylene	P
		n-but-1-ene	m
14	VII	ethylene	P
		n-but-1-ene	m
15,16.	VIII	methane	P
19,20.	X	methane	P
		ethane	P
		ethylene	P
		propene	t
23,24.	XI	methane	P
		ethane	P
		n-butane	t
		ethylene	P
		propene	t
27,28.	XII	methane	P
		propane	m
		ethylene	P
		propene	t
29,30.	XIII	methane	P
		ethylene	P
		propene	t

Note: ethylene is omitted where it is the sole olefinic component.

Abbreviations: P ... a principal olefinic or saturated gas

m ... a minor " " " "

t ... a trace " " " "

Table 8 (cont.) - Qualitative Infrared Analysis of Gases.

Run No.	Pyrolysand	Gas Identified	Relative Quantity
31.	XIV	methane	P
		propane	m
		ethylene	P
		propene	m
		methylacetylene	t
32	XV	methane	P
		ethane	P
		ethylene	P
		propene	t
44,45.	XXI	ethylene	m
		propene	P
		methylacetylene	m
47,48.	XXII	methane	P
52,53.	XXV	ethylene	m
		propene	P
		methylacetylene	m

Note: ethylene is omitted where it is the sole olefinic component.

Table 9 - Retention Volumes of Comparison Standards.

Column temperature	62.5°			78°			92°		
	R_t	V_r	V_r^o	R_t	V_r	V_r^o	R_t	V_r	V_r^o
Propionaldehyde	2.24	11.16	5.35	2.23	7.71	5.24	1.95	5.79	4.20
Acrolein	2.4	11.99	5.75	2.31	8.01	5.45	1.95	5.79	4.20
n-butyraldehyde	5.7	28.5	13.67	4.63	16.0	10.89	3.78	11.2	8.15
iso-butyraldehyde	2.87	14.3	6.89	2.6	9.04	6.15	2.52	7.5	5.43
Crotonaldehyde	9.5	47.4	22.75	7.0	24.4	16.55	5.31	15.8	11.45
α-Methylacrolein	5.21	26.0	12.47	3.54	12.25	8.34	2.8	8.31	6.06
n-Valeraldehyde	12.9	64.1	30.95	11.0	38.0	25.95	8.66	25.7	18.67
Acetaldehyde							0.69	2.04	1.48
Methyl formate	1.75	8.7	4.19	1.69	5.86	3.99	1.22	3.6	2.61
Methyl acetate	3.49	17.4	8.35	3.1	10.8	7.31	2.3	6.81	4.95
Methyl propionate	7.66	38.1	18.35	6.32	22.0	14.95	5.01	14.9	10.81
Methyl n-butyrate	16.2	80.7	38.75	12.0	41.7	28.45	8.92	26.5	19.25
Methyl iso-butyrate				9.6	33.2	22.55	7.36	21.9	15.85
Methyl acrylate	6.62	33.0	15.85	5.5	19.1	13.0	4.48	13.3	9.67
Methyl crotonate	23.55	117.6	56.45	16.62	57.8	39.25	12.03	35.9	26.0
Methyl α-methylacrylate	15.16	73.35	36.25	11.7	39.9	27.05	8.69	25.1	18.72
Methyl vinylacetate	5.08	25.3	12.19	4.18	14.46	9.85	3.42	10.16	7.39
Methyl allylacetate	11.6	57.9	27.74	8.8	30.5	20.75			
Ethyl formate				2.44	8.43	5.73			
Ethyl acrylate				9.0	31.25	21.25	8.21	24.6	17.89
Methanol	1.37	6.81	3.28	1.22	4.22	2.87	0.97	2.89	2.1
Ethanol				2.11	7.32	4.99	1.82	5.4	3.94
n-Propanol				3.93	13.6	9.27			
n-butanol				8.82	30.6	20.85			
iso-butanol				6.6	22.8	15.55			
Propyrgyl alcohol				4.1	14.2	9.65			
Acetone				1.98	6.87	4.66			
Diethyl ketone				5.3	18.33	12.45			
Methyl ethyl ketone				4.45	15.4	10.49			
Methyl vinyl ketone				4.1	14.2	9.65			
n-octane	34.5	171.7	82.45	19.14	66.3	45.05	17.42	51.9	37.55
n-hexane	6.04	30.1	14.45	20.6	71.8	48.75			
n-octene				6.9	23.9	16.25			
n-hetpene				24.5	84.5	57.55			
n-hexene				4.6	16.0	10.85			

Table 9 (cont.) - Retention Volumes of Comparison Standards.

Column temperature	140°			150°			159°		
	R_t	V_r	V_r^o	R_t	V_r	V_r^o	R_t	V_r	V_r^o
Methyl succinate							25.0	71.0	53.9
Methyl glutarate							14.5	53.9	35.5
Methyl adipate							9.38	34.8	23.0
Methyl sebacate				8.5	84.5	22.1	8.8	32.6	21.6
Methyl n-nonoate	30.45	184.0	83.2	22.5	128.0	58.1	23.5	66.2	50.1
Methyl n-heptoate	10.62	64.2	29.15	8.43	48.1	21.95	8.5	24.4	18.5
n-butyraldehyde							1.5	4.25	3.22
n-valeraldehyde							1.56	7.18	3.0
n-heptaldehyde	6.58	30.6	14.0	5.15	29.4	13.37	4.1	18.8	7.89
n-hexane	1.72	8.0	3.65	1.44	8.2	3.74	1.31	5.99	2.5
n-heptane	2.47	11.54	5.27				1.88	8.6	3.6
n-octane	4.1	19.1	8.72	3.09	17.6	8.0	2.8	12.8	5.39
n-decane				8.4	47.9	21.6			

Table 10 - Analysis of Pyrolysates by Gas-liquid Chromatography.

Methyl succinate pyrolysate; fraction 70 - 88° + cold trap liquid.

Column Temp.:	62.5°			78°			92°		
	R_t	V_r	V_r^o	R_t	V_r	V_r^o	R_t	V_r	V_r^o
i	1.39	6.91	3.33	1.27	4.34	3.01	-	-	-
ii	1.75	8.7	4.19	1.69	5.78	4.01	1.23	4.02	2.71
iii	2.28	11.36	5.44	2.16	7.4	5.15	1.84	5.95	4.05
iv	2.57	12.8	6.15	-	-	-	-	-	-
v	3.44	17.06	8.2	3.05	10.4	7.25	2.65	8.65	5.83
vi	6.59	32.75	15.75	5.49	18.7	13.0	4.39	14.34	9.68
vii	7.62	38.0	18.25	6.27	21.4	14.86	-	-	-
viii	15.8	78.9	37.95	12.36	42.1	29.35	8.91	29.1	19.65

Methyl methylsuccinate pyrolysate; fraction 80 - 105° + cold trap liquid.

i	1.36	6.77	3.25	1.275	4.69	3.05	-	-	-
ii	1.96	9.74	4.69	1.62	6.0	3.85	1.13	3.72	2.7
iii	2.85	14.22	6.86	2.72	10.02	6.45	2.2	7.21	5.25
iv	3.61	18.0	8.68	3.24	11.93	7.68	2.45	8.04	5.83
v	7.09	35.2	16.95	5.86	21.6	13.85	4.13	13.6	9.87
vi	8.5	42.5	20.45	6.89	25.4	16.25	-	-	-
vii	12.18	60.6	29.05	9.74	36.0	23.05	6.99	21.55	15.65
viii	15.2	71.9	36.45	11.46	42.4	27.15	-	-	-
ix	16.2	80.7	38.65	12.3	45.4	29.05	7.9	26.0	18.85
x	18.53	92.2	44.45	14.4	53.0	34.05	9.39	30.9	22.45
xi	23.11	115.4	55.45	16.8	62.0	39.95	10.6	34.9	25.35

Methyl glutarate pyrolysate; fraction 69 - 90° + cold trap liquid.

i	1.42	6.96	3.35	1.21	4.19	2.85	.966	3.0	2.1
ii	1.97	8.69	4.19	1.654	5.71	3.9	1.276	3.95	2.77
iii	2.6	12.78	6.14	2.78	9.63	6.57	1.93	6.0	4.2
iv	3.45	16.9	8.15	3.58	12.4	8.45	2.22	6.9	4.84
v	5.53	27.1	13.08	4.53	15.7	10.69	3.8	11.79	8.25
vi	6.63	32.5	15.7	5.61	19.45	13.25	4.49	13.92	9.75
vii	11.1	54.5	26.25	8.28	28.6	19.55	-	-	-
viii	11.8	58.0	27.95	12.19	42.15	28.75	8.5	26.4	18.45
ix	22.55	111.0	53.45	14.78	51.1	34.95	12.55	39.0	27.35

Table 10 (cont.) - Analysis by Gas-liquid Chromatography.

Methyl adipate pyrolysate; fraction 66 - 102° + cold trap liquid.

Column Temp.:	62.5°			78°			92°		
	R_t	V_r	V_r^o	R_t	V_r	V_r^o	R_t	V_r	V_r^o
i	1.35	6.71	3.24	1.3	4.45	3.1	.995	3.11	2.17
ii	1.775	8.79	4.25	1.68	5.71	3.99	1.46	4.56	3.19
iii	2.24	11.12	5.35	2.42	8.27	5.75	2.21	6.92	4.48
iv	2.56	12.8	6.14	-	-	-	-	-	-
v	3.525	17.6	8.44	3.18	10.82	7.55	2.5	7.81	5.45
vi	6.54	32.55	15.67	5.41	18.7	12.85	4.9	15.3	10.65
vii	7.61	38.0	18.25	6.1	20.8	14.45	-	-	-
viii	16.0	79.5	38.25	11.93	40.6	28.35	9.04	28.3	19.74
ix	21.6	107.9	51.95≠	16.4	56.0	38.95	11.76	36.75	25.55
x	25.6	127.7	61.25≠	19.55	66.8	46.45	14.58	45.5	31.75
xi	67.1	158.3	76.15≠	23.4	79.8	55.45	23.5	51.1	35.85

Methyl sebacate pyrolysate; fraction 72 - 100° + cold trap liquid.

i	1.39	6.96	3.33	1.17	4.25	2.89	-	-	-
ii	1.775	8.89	4.25	1.5	5.27	3.58	1.31	4.16	2.9
iii	2.275	11.2	5.44	2.16	7.59	5.16	1.99	6.31	4.4
iv	3.7	18.47	8.85	3.05	10.63	7.25	2.36	7.51	5.23
v	6.62	35.2	16.85	5.42	19.0	12.95	4.4	14.0	9.73
vi	11.0	55.1	26.45≠	-	-	-	-	-	-
vii	12.17	60.9	29.05≠	-	-	-	-	-	-
viii	16.2	81.0	38.75	11.7	41.0	27.95	9.18	29.1	20.35
ix	24.5	122.0	58.45≠	-	-	-	-	-	-
x	33.6	168.0	80.45	20.5	71.8	48.75	17.95	57.0	39.65

Methyl succinate + hydroquinone pyrolysate; fraction 68 - 85° + cold trap liquid.

i	1.35	6.71	3.24	-	-	-
ii	1.762	8.8	4.24	1.334	4.7	3.24
iii	2.15	10.7	5.15	-	-	-
iv	2.56	12.79	6.13	2.405	8.5	5.85
v	3.39	16.82	8.1	2.95	10.4	7.15
vi	6.65	33.1	15.95	5.09	17.98	12.35
vii	7.56	37.6	18.1	6.4	22.55	15.55
viii	10.4	51.9	24.95	9.85	34.8	23.95
ix	16.0	79.6	38.25	11.42	40.4	27.75

≠ approximate values for trace components.

Table 10 (cont.) - Analysis by Gas-liquid Chromatography.

Methyl propionate pyrolysate; total liquid.

Column Temp.:	62.5°			78°			92°		
	R_t	V_r	V_r^o	R_t	V_r	V_r^o	R_t	V_r	V_r^o
i	1.39	6.91	3.33	1.2	4.05	2.84	.94	2.96	2.06
ii	1.65	8.21	3.95	1.55	5.23	3.66	1.24	3.9	2.71
iii	2.11	10.56	5.07	2.155	7.29	5.1	1.87	5.9	4.1
iv	3.54	17.6	8.46	3.16	10.66	7.49	-	-	-
v	-	-	-	3.58	12.05	8.45	3.09	9.61	6.7
vi	7.62	38.0	18.25	6.3	21.2	14.84	5.06	15.96	11.1
vii	15.79	78.4	37.7 n	-	-	-	9.9	31.2	21.7

Methyl vinylacetate pyrolysate; total liquid.

i	1.335	6.67	3.2	-	-	-
ii	1.64	8.21	3.95	1.49	5.15	3.55
iii	2.31	11.56	5.55	1.975	6.81	4.7
iv	5.1	25.5	12.25	4.21	6.1	10.05
v	6.25	52.1	25.05n	-	-	-

Methyl allylacetate pyrolysate; total liquid.

i	1.335	6.67	3.2	-	-	-
ii	1.64	8.21	3.95	-	-	-
iii	2.69	9.39	6.48	2.51	8.9	6.13
iv	5.41	18.93	13.05	4.61	16.39	11.27
v	11.4	39.6	27.45	8.55	30.3	20.95

Methyl n-heptoate pyrolysate; fraction 68 - 80° + cold trap liquid.

i	-	-	-	.53	2.92	1.416
ii	1.29	5.29	3.3	.92	5.09	2.45
iii	1.53	6.28	4.0	1.21	6.7	3.24
iv	2.64	10.78	7.27	1.31	7.23	3.5
v	3.06	12.56	8.56	3.12	17.2	8.31
vi	5.82	23.95	16.85	5.58	30.7	14.81
vii	8.92	36.5	26.05	7.57	41.8	20.2
viii	12.27	51.1	36.55	13.63	75.3	36.5
ix	20.3	83.2	60.25	16.53	85.9	41.5
x	26.7	109.4	79.25			

Table 10 (cont.) - Analysis by Gas-liquid Chromatography.

Methyl n-nonoate pyrolysate; fraction 62 - 78° + cold trap liquid.

Column Temp.:	62.5°			78°			92°		
	R_t	V_r	V_r^o	R_t	V_r	V_r^o	R_t	V_r	V_r^o
i	1.39	5.72	3.45	1.01	4.15	2.59			
ii	1.56	6.41	3.98	1.5	6.17	3.85			
iii	-	-	-	1.97	10.87	5.28			
iv	3.29	13.58	8.46	2.81	15.55	7.51			
v	5.12	21.15	14.1	3.79	21.0	10.6			
vi	5.79	23.9	16.08	3.63	20.0	13.0			
vii	8.8	36.1	24.6	5.93	32.8	21.3			
viii	12.0	59.2	33.8	7.7	42.5	27.6			
ix	28.2	115.9	80.2	12.6	69.7	45.2			
x	-	-	-	34.05	188.0	91.0			

Methyl sebacate pyrolysate; fraction >100°.

Column Temp.:	150°			159°		
i	2.96	17.4	7.9	2.14	8.41	5.5
ii	5.08	29.8	13.54	3.14	12.4	8.1
iii	-	-	-	5.6	20.75	13.74≠
iv	8.4	47.9	21.8	8.8	32.6	21.6
v	14.8	84.2	38.4	13.38	49.5	32.8

Methyl n-heptoate pyrolysate; fraction 158 - 170°.

Column Temp.:	140°			159°		
i	4.04	24.45	11.25	2.19	10.02	4.2
ii	-	-	-	3.04	13.92	5.8≠
iii	5.08	30.6	13.83	4.11	18.9	7.83
iv	6.4	38.75	17.56	-	-	-
v	10.57	63.9	28.96	9.86	45.1	18.6
vi	17.74	107.4	48.5	-	-	-

≠ approximate values for trace components.

Table 10 (cont.) - Analysis by Gas-liquid Chromatography.

Methyl n-nonoate pyrolysate; fraction 160 - 195°.

Column Temp.:	140°			159°		
	R_t	V_r	V_r^o	R_t	V_r	V_r^o
i	3.1	18.79	8.5	2.7	12.4	5.2
ii	4.35	26.4	11.94	4.44	20.4	8.53
iii	6.93	42.0	19.01	-	-	-
iv	10.82	66.0	29.8	9.4	43.25	18.1
v	20.1	122.0	55.15	11.2	51.2	21.5
vi	30.5	184.3	83.8	25.9	119.0	49.8

Note: The higher boiling fractions of the pyrolysates from methyl succinate, glutarate, adipate and methylsuccinate contained only unchanged pyrolysand in detectable quantity.

Table 11 - 'Onset' Temperatures.

Pyrolysand	Sample g.	Detection Reagent	'Onset' Temperature	Reactor Volume
VIII	0.25	Br_2/CCl_4	325	50 ml.
"	0.5	"	327	"
"	1.0	"	343	"
"	1.5	"	351	"
X	0.25	2:4-DNP/HCl	482	"
"	0.75	"	490	"
"	1.0	"	493	"
"	1.5	"	529	"
XII	0.25	"	469	175 ml
"	0.75	"	473	"
"	1.5	"	471	"
"	0.25	"	469	50 ml.
I	"	Br_2/CCl_4	364	"
V	"	"	348	"
Ethyl suberate	"	"	373	"
XI	"	2:4-DNP/HCl	463	"
XIII	"	"	402	"
X	"	"	485	175 ml
XI	"	"	458	"
XIII	"	"	399	"
Methyl pimelate	"	"	442	"
+ 3 % Benzoyl Peroxide.				
X	"	"	395	"
XII	"	"	410	"
XI	"	"	385	"
Methyl pimelate	"	"	378	"
XIII	"	"	361	"

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